

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

CORROSIVITY OF KRAFT LIQUORS

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to

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CORROSIVITY OF KRAFT LIQUORS

SUMMARY

The aim of this work was to characterize the metal/environment system of the kraft liquor. This was accomplished by reviewing the chemistry of wood, the interactions between wood species and the cooking liquor, and the composition of white, green, and black liquors. The electrochemical processes responsible for the corrosive attack in kraft liquors were discussed.

It has been shown that an increase in NaOH and Na₂S concentrations impaired the ability of mild steel to become passive.

The anodic polarization behavior of mild steel in white liquor showed a dominant effect of sulfide ions over thiosulfate ions; it appeared as if sulfide ions were preferentially adsorbed.

Little attention has been given to the effect of the organic species originating from wood on the electrochemical and corrosion behavior of steel. The role of catechol in increasing the corrosion rate of steel was identified with weight loss measurements. The corrosive action of catechol was attributed to the presence of two adjacent hydroxyl groups which made catechol capable of forming soluble organometallic complexes in the steel. Little change in the corrosion rate of mild steel was observed when pyrogallol was added to a NaOH solution, whereas the addition of pyrogallol to white liquor caused a significant increase in the corrosion rate of steel. These two studies on catechol and pyrogallol are among the very few published on the role of organic species on the electrochemical behavior of mild

steel, and it became clear from the literature review that a significant void exists regarding studies with organic species in kraft liquors.

INTRODUCTION

For the past 30 years, corrosion studies in kraft liquor systems were conducted. The 1950's may be considered the golden era for corrosion studies; numerous publications with excellent results came out during this period. For example, a hypothetical model was proposed to relate the corrosion rate of mild steel in kraft liquors to liquor composition, via a corrosivity equation. Reactions responsible for the corrosive attack on mild steel in white liquor were also identified. The influence of steel composition on the corrosion rate of steel was studied by Von Essen (1). He reported that the high silicon content (0.2% Si) of the newly developed killed steels, as compared to 0.005% Si in older rimmed steels, was contributing to increased corrosive attack. This finding was confirmed by Huseby and Scheil (2), Hopper (3), Shoumatoff and Teeple (4), Hassler (5), and Roald (6).

The attention that the corrosion studies had in the 1950's seemed to fade away in the 1960's. However, in the 1970's, the awareness of corrosion problems in kraft liquors has grown significantly. The awareness may be attributed either to the significant cost that the paper industry suffered from corrosion problems and/or to the campaign that corrosion experts have embarked on to enlighten the paper industry to the danger of corrosion. The result of this awareness manifests itself in the devotion of major research programs to studying corrosion in kraft liquor systems from a fundamental point of view. Two major research programs are already underway: The MacMillan Bloedel (MB) research program headed by Bob Charlton and Don Wensley, and The Institute of Paper Chemistry research program financed by the Fourdrinier Kraft Board Group and The Institute of Paper Chemistry and headed by David Bowers and Nadia Tonsi-Eldakar. The first program, which has been in progress for some time, has resulted in the publication of an interesting paper given by Charlton and Wensley at the NACE meeting in Atlanta, Georgia, early this year (7). The first fruit of our research

program is this report. The report is a literature review on the significant findings of the most pertinent corrosion and electrochemical studies done in kraft liquor systems as well as related systems.

ELECTROCHEMICAL BEHAVIOR OF A METAL

The electrochemical behavior of a metal may be described by the cathodic and anodic polarization curves of the metal.

CATHODIC BEHAVIOR

The rate of the cathodic reaction may be controlled by activation and/or concentration polarization.

Concentration Polarization

Figure 1 shows the polarization curve of a cathodic reaction which is controlled by concentration polarization.

The phenomenon of concentration polarization is illustrated by Fig. 2. As can be seen at low reduction rates, the distribution of positive ions at the electrode-electrolyte interface is relatively uniform. However, at high reduction rates, the interface is approximately depleted by positive ions. As the reduction rate is increased further, the rate of the reduction will be controlled by the rate of diffusion of positive ions to the electrode surface. The highest rate at which the ions are transferred to the electrode surface is called the limiting diffusion rate or limiting diffusion current. The limiting diffusion current density, I_L , may be expressed as

$$I_L = \frac{DnFC_B}{\delta}$$

where D is the diffusion coefficient of the reacting species, which in this case is the positive ions, C_B is the bulk concentration of the reacting species, and δ is the thickness of the diffusion layer.

The above equation illustrates that I_L is a function of D , C_B , and δ . Thus, changes that affect these parameters will affect I_L . It is generally noticed that there

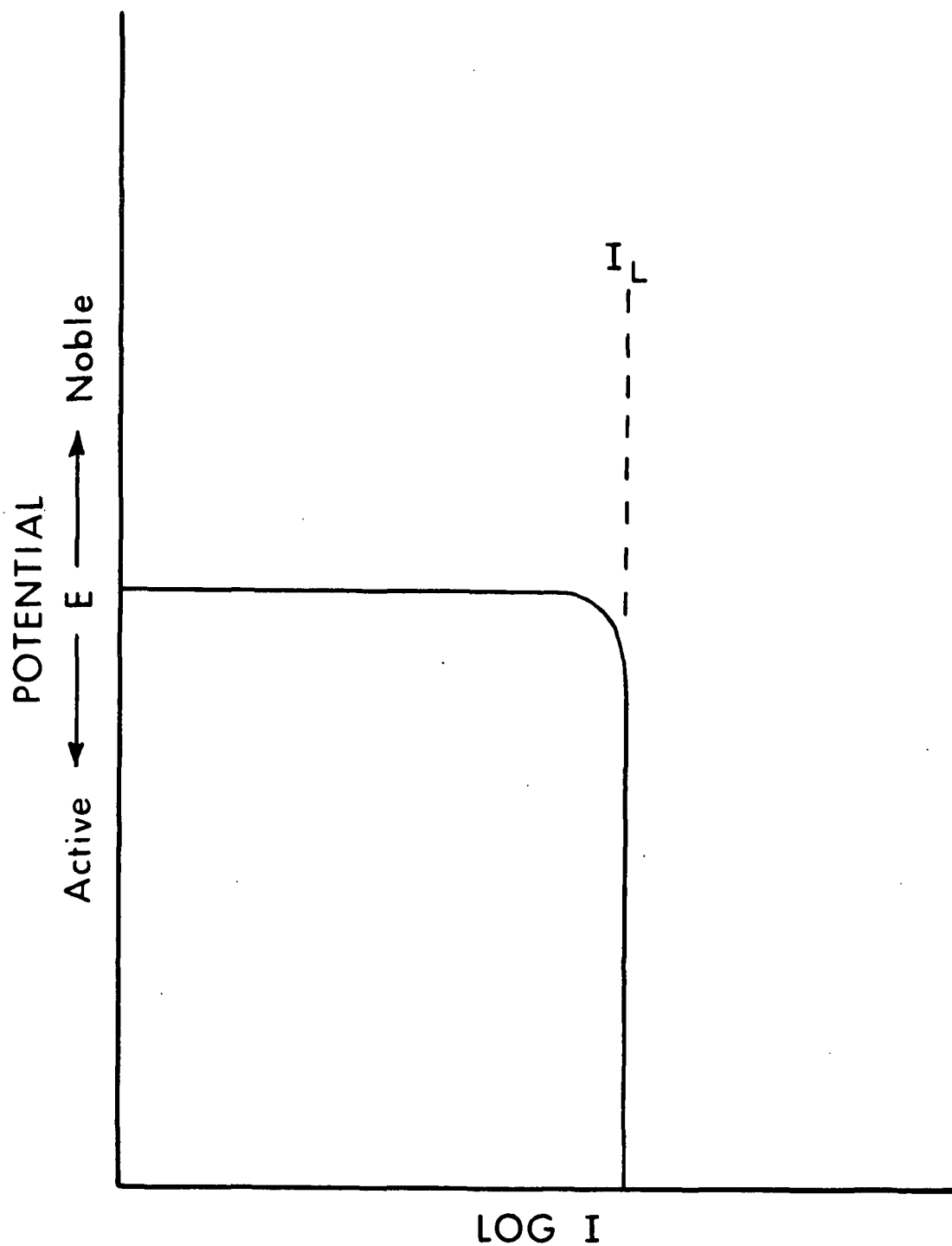


Figure 1. Concentration Polarization Curve

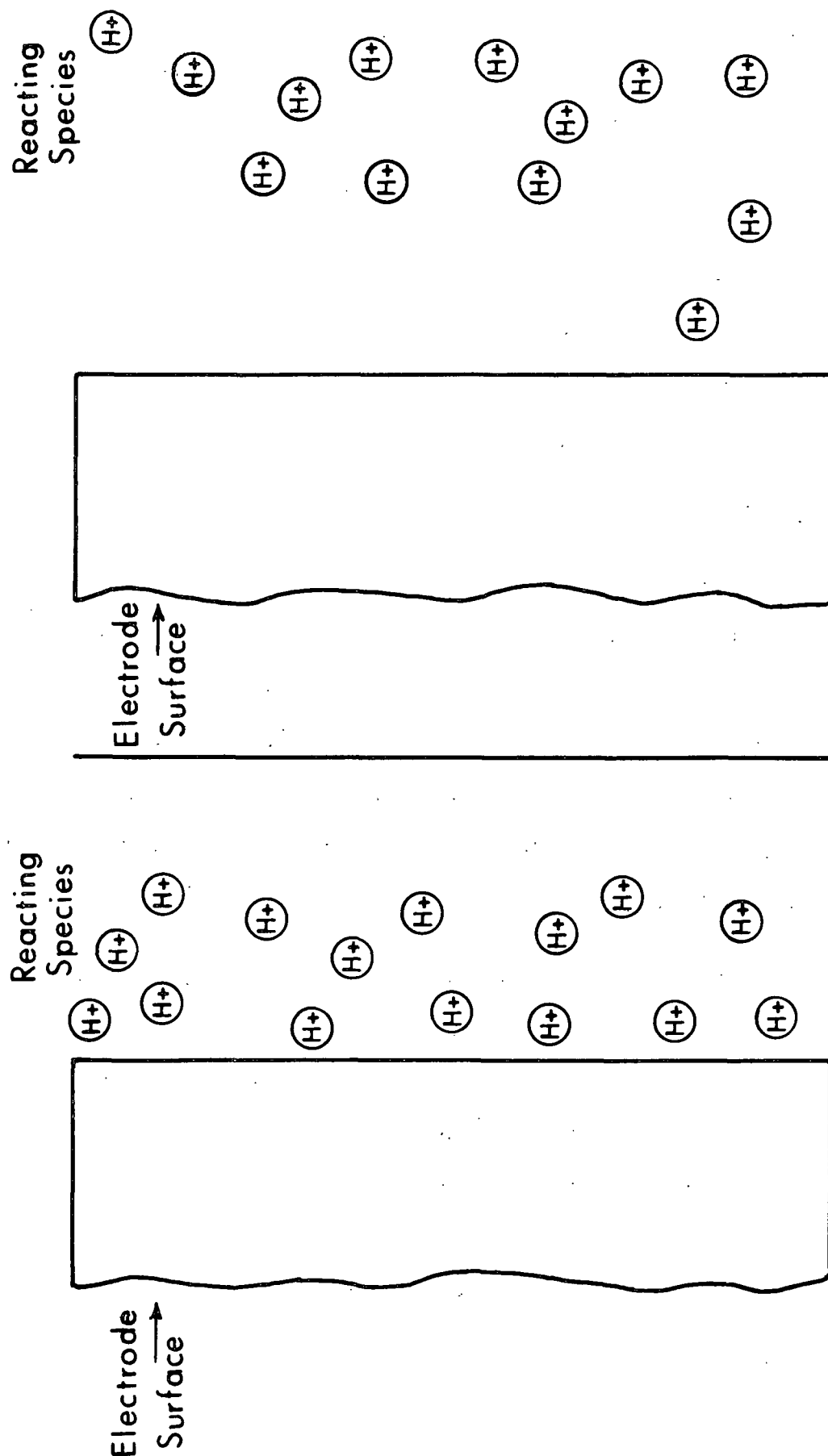


Figure 2. Schematic Diagram for Concentration Polarization Phenomenon

is a linear relationship between the concentration of reacting ions in solution and I_L . The thickness of the diffusion layer is influenced by agitation. Agitation or stirring of the electrolyte tends to reduce δ and, therefore, increase I_L . The effect of these variables on concentration polarization is shown in Fig. 3.

It is very important to note that I_L is usually only significant during reduction processes and is usually negligible during metal dissolution reactions. The reason behind it is that there is an almost unlimited supply of metal atoms for dissolution.

Activation Polarization

The cathodic reaction may be also controlled by activation polarization as seen in Fig. 4. In other words, the rate of the cathodic reaction is determined by the charge transfer across the electrode-electrolyte interface. Within the activation-controlled region, the relationship between the electrode potential and the logarithm of the current is a linear one. The linear region is also termed the Tafel region. The slope of the Tafel region is called the Tafel slope. The derivation of the Tafel slope is given in detail in the Appendix (p. 70).

The rate of the reduction reaction controlled by activation polarization is also affected by the increase in the concentration of the reacting species and temperature. Figure 5 illustrates the effect of increasing concentration on the cathodic polarization of a metal. The increase in the concentration of the reacting species and in temperature causes a shift in the cathodic polarization curve toward more noble potentials. The shift is frequently referred to as a decrease in cathodic polarization. Also, a shift toward more negative potentials is called an increase in cathodic polarization.

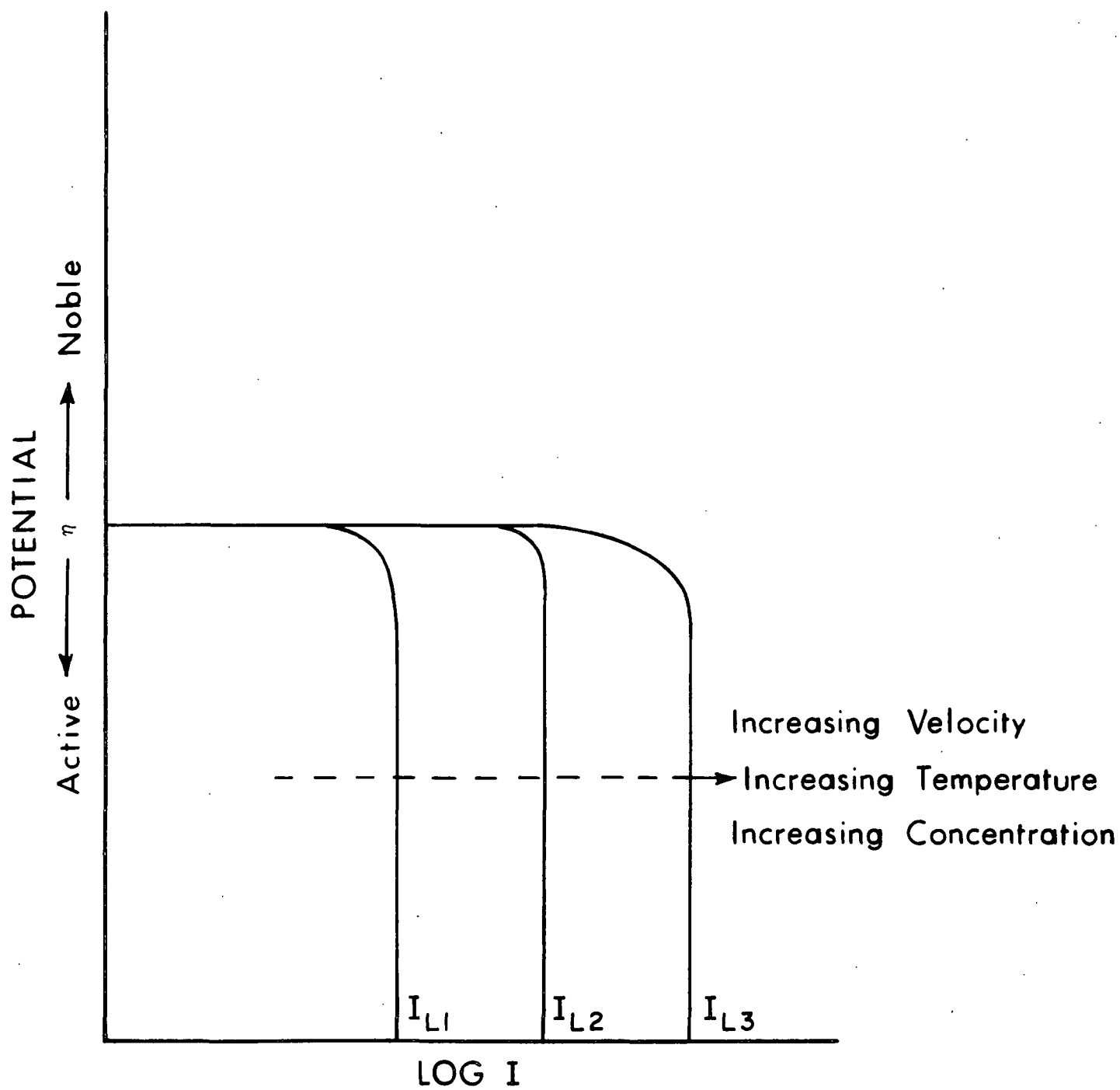


Figure 3. Effect of Environmental Variables on Concentration Polarization Curve

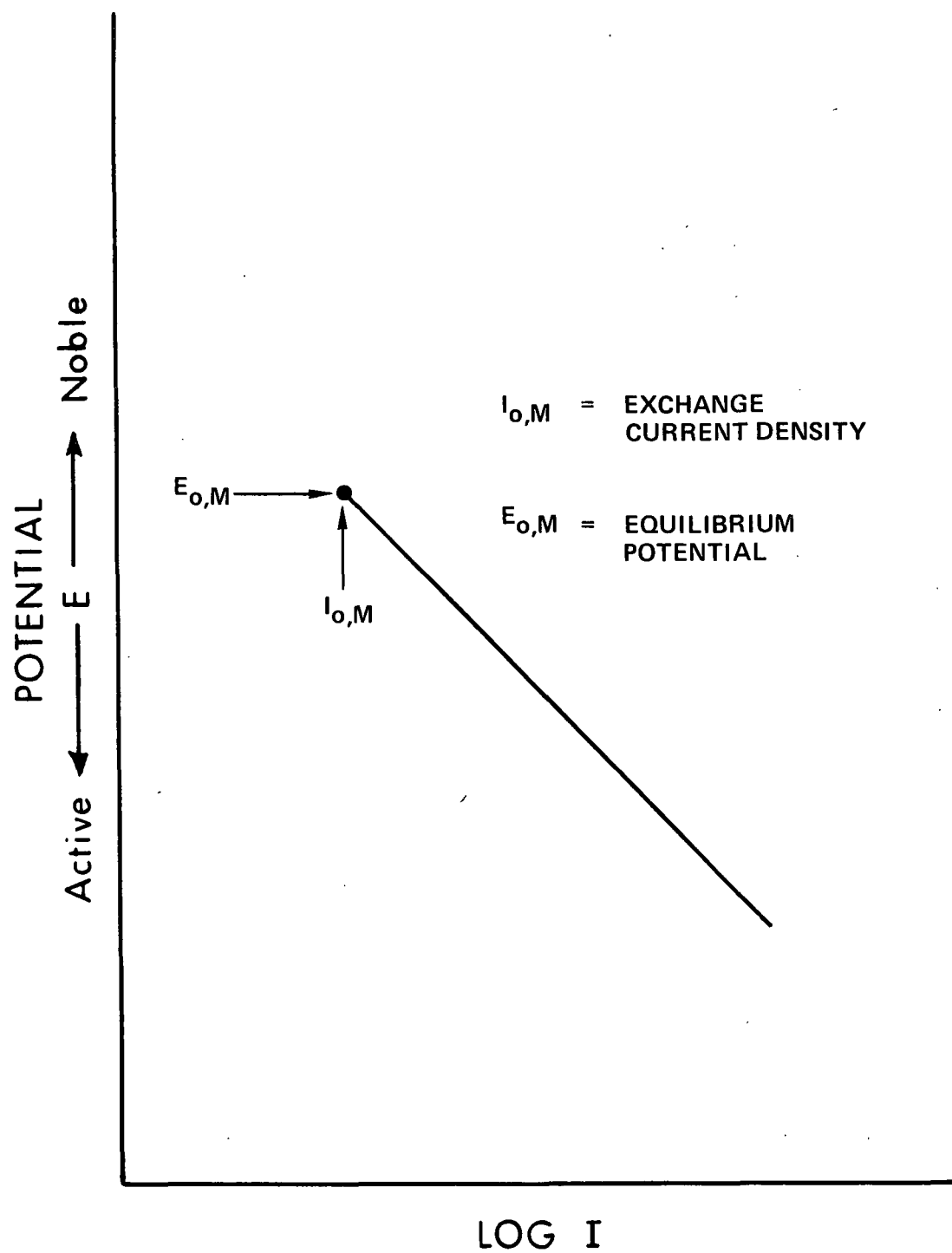


Figure 4. Activation Polarization Curve

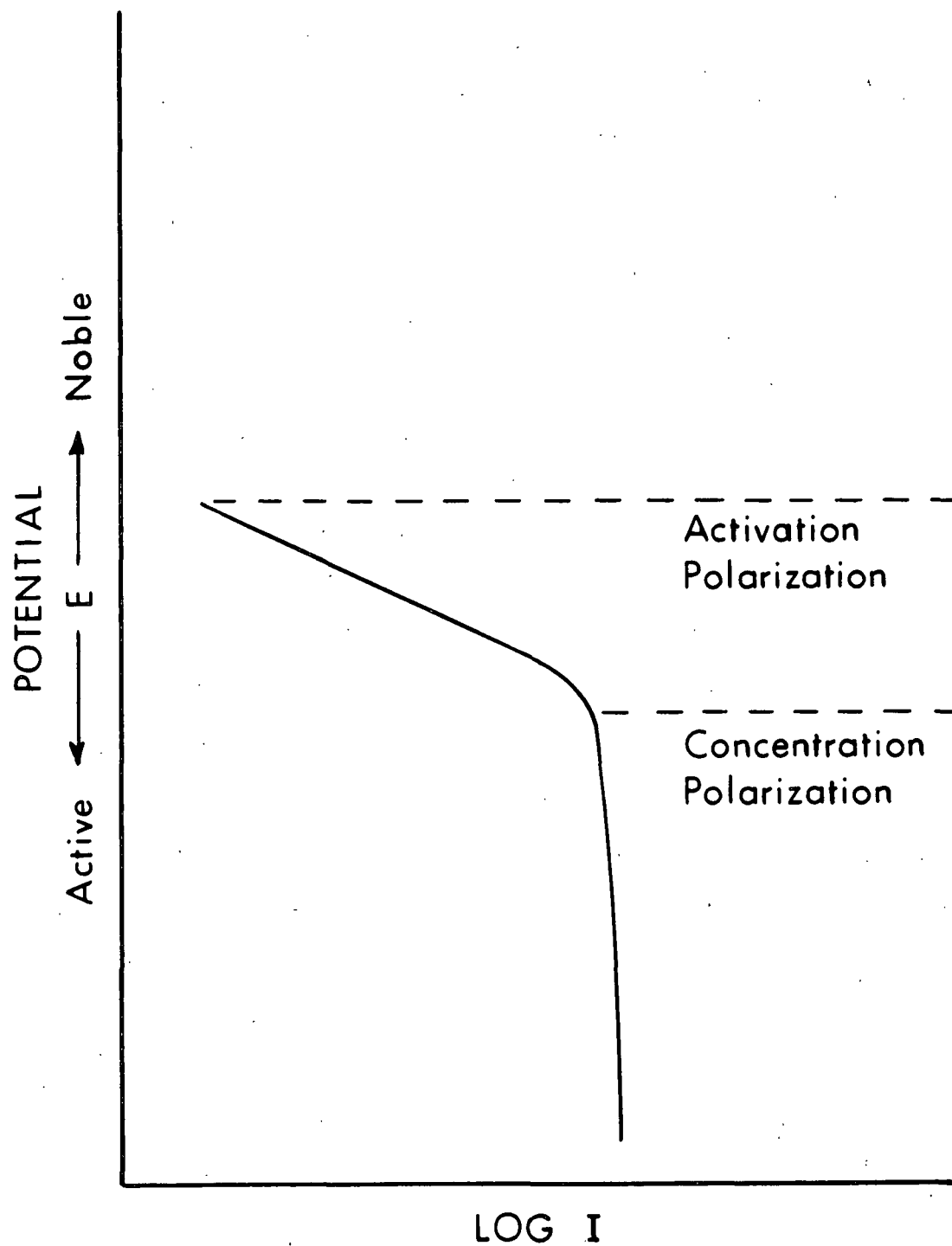


Figure 5. Combined Polarization Curve (Activation and Concentration Polarization)

It is very important to note that the rate of the reaction which is activation controlled is not affected by agitation or stirring, unlike the rate of the reaction which is controlled by concentration polarization. Thus, agitation or stirring effects may be used to determine if the rate of a reaction is activation- or concentration-polarization controlled.

Combined Polarization

Both activation and concentration polarization usually occur at the metal surface. Activation polarization usually dominates at low reaction rates, while concentration polarization dominates at higher rates. A combined cathodic polarization curve can be seen in Fig. 5.

ANODIC BEHAVIOR

Figure 6 illustrates the typical behavior of an active-passive metal. Initially, as the electrode potential is anodically increased, the dissolution rate of the metal increases exponentially. The relationship between the electrode potential and the logarithm of the current density displays a typical Tafel behavior. The region which shows the Tafel behavior is called the active region. As can be seen from Fig. 6, the active region is observed until a certain critical potential is reached. The critical potential, E_{pp} , is also known as the primary passive potential. The corresponding current is known as the critical anodic current for passivity I_{crit} . That part of the curve at which the current and potential reach some critical value is called the current density maximum. More than one current density maximum may be encountered, depending on the metal and on the environment. The most significant of these maxima is usually the one with the highest magnitude of current density, referred to as I_{crit} .

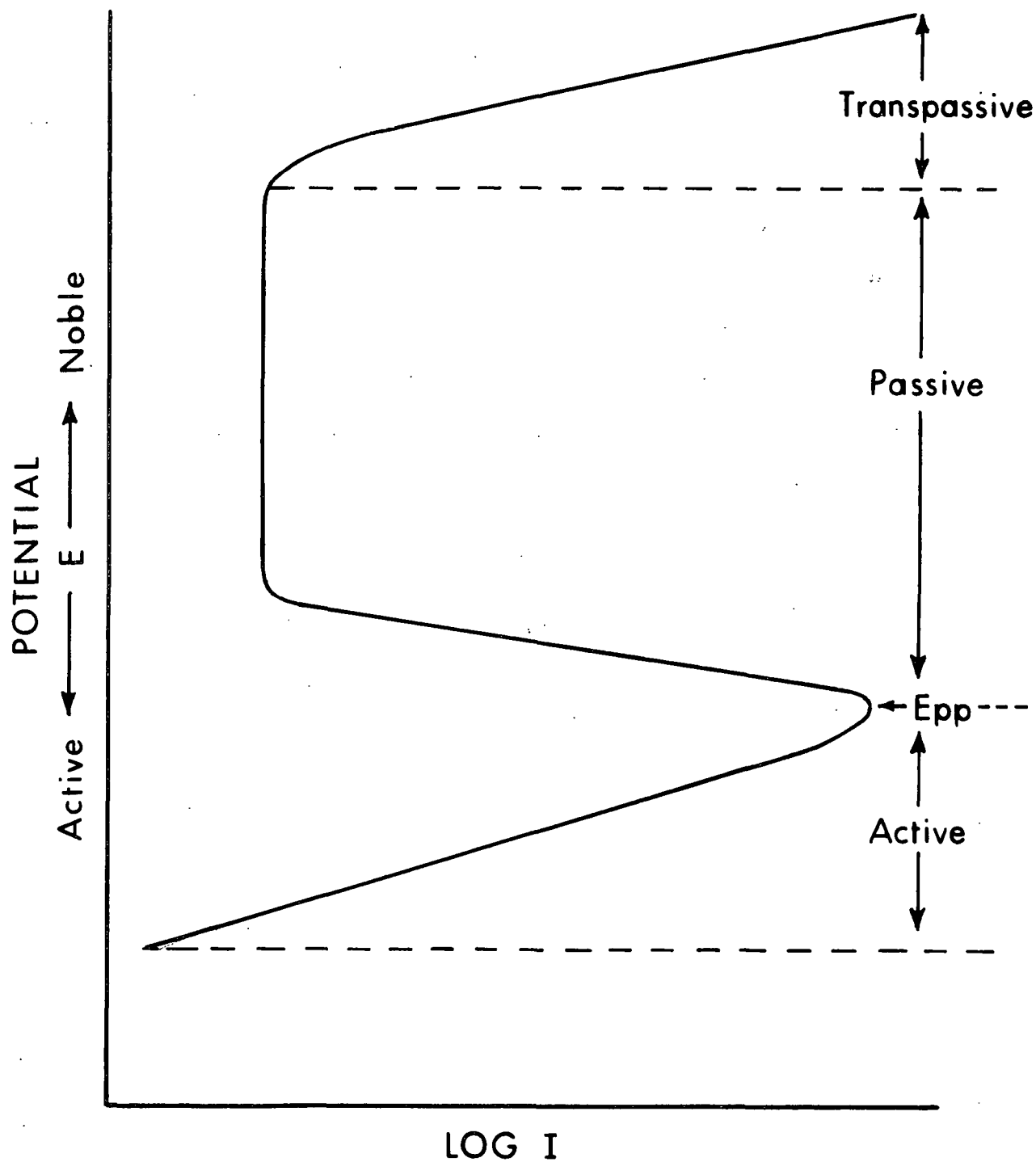


Figure 6. Typical Anodic Behavior of an Active-passive Metal

Beyond the critical potential, the dissolution rate drops sharply. The decrease in the dissolution rate is the result of film formation at the critical potential, E_{pp} . Following the drop, the dissolution rate remains independent of potential over a considerable potential region. This region is termed the passive region.

Beyond the passive region, further increase in the electrode potential is associated with an increase in the current. This region is known as the trans-passive region. The increase in the current may be due to another process occurring at the electrode surface, for example oxygen evolution, or to the conversion of the passive film into a higher valence state which is soluble and permits free dissolution of the metal to occur again.

THE EXPERIMENTAL SET-UP

ELECTROCHEMICAL CELL

The electrochemical characteristics of a metal may be studied with a three-electrode system. These electrodes are arranged in an electrochemical cell as shown in Fig. 7. The test (working) electrode is the material under investigation. The auxiliary (counter) electrode is generally made of platinum. The reference electrode is an unpolarizable electrode of known potential, e.g., saturated calomel electrode (SCE). The Luggin capillary is used to minimize the introduction of IR drops in the potential measurements. In addition, the cell can be thermostated to maintain a constant temperature, and additional parts can be built into the cell to introduce deaerated gases as shown in Fig. 7.

ELECTROCHEMICAL TECHNIQUES

The polarization curves which describe the electrochemical behavior of the metal for a given environment may be obtained by galvanostatic or potentiostatic methods. Both methods are used to obtain the potential-current relations (polarization curves). The difference between these methods is the choice and control of the independent variables. In galvanostatic polarization the independent variable is the current, whereas in the potentiostatic method the independent variable is the electrode potential. As long as the polarization curve does not contain a negative loop, either method can be used equally well. The "negative loop" describes the behavior of the electrode in which, at first, with increasing electrode potential, the current increases and then, after reaching a critical value, further increase of potential causes a decrease in current. If the galvanostatic technique is used to determine the polarization curve shown in Fig. 8, the potential will increase with each increase in current until the I_{crit} is exceeded. Subsequent increase in current shifts the potential to a large positive value which is indicated by dashes in Fig. 9.

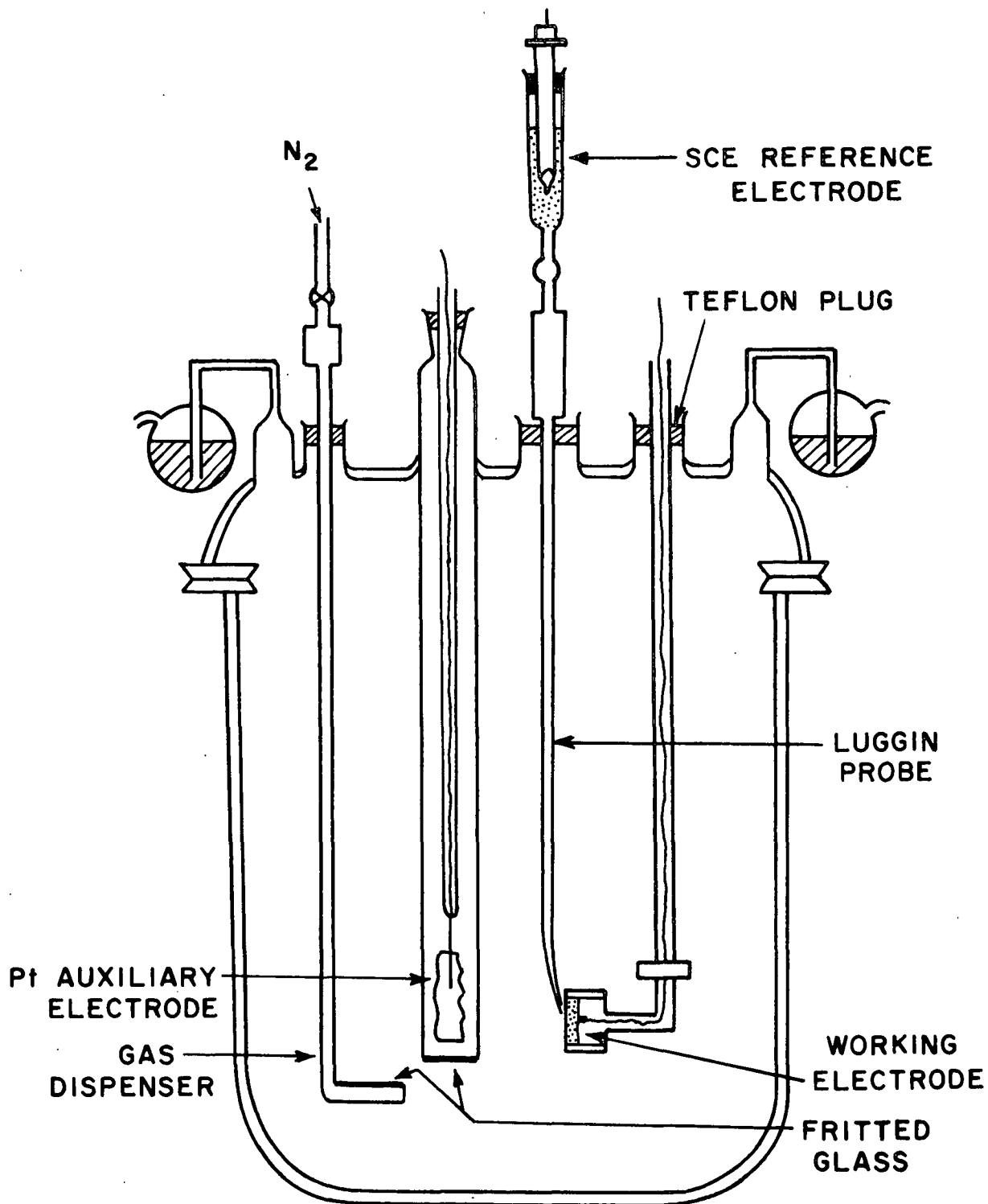


Figure 7. An Electrochemical Test Cell

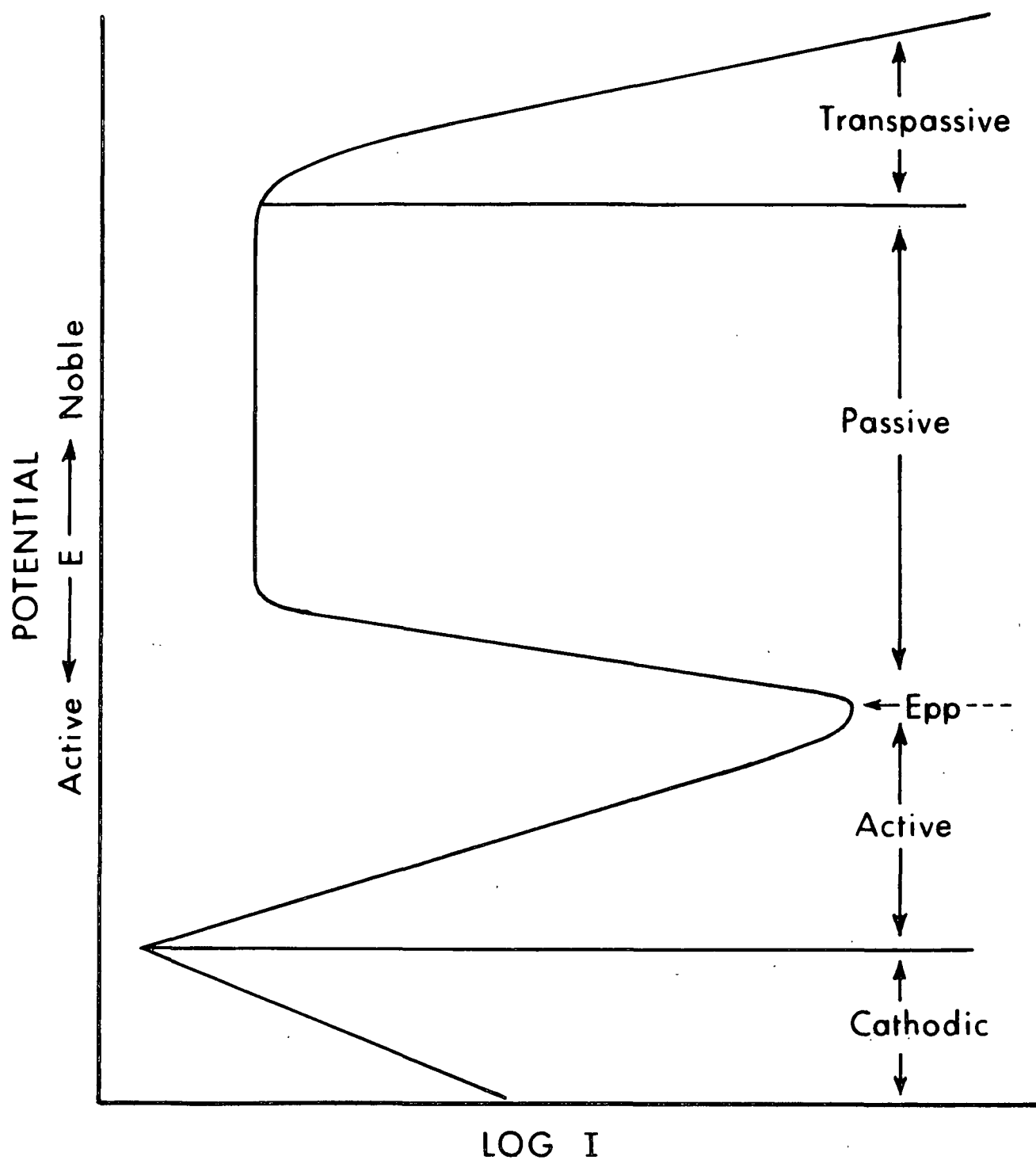


Figure 8. Potentiostatic Polarization Curve of an Active-passive Metal

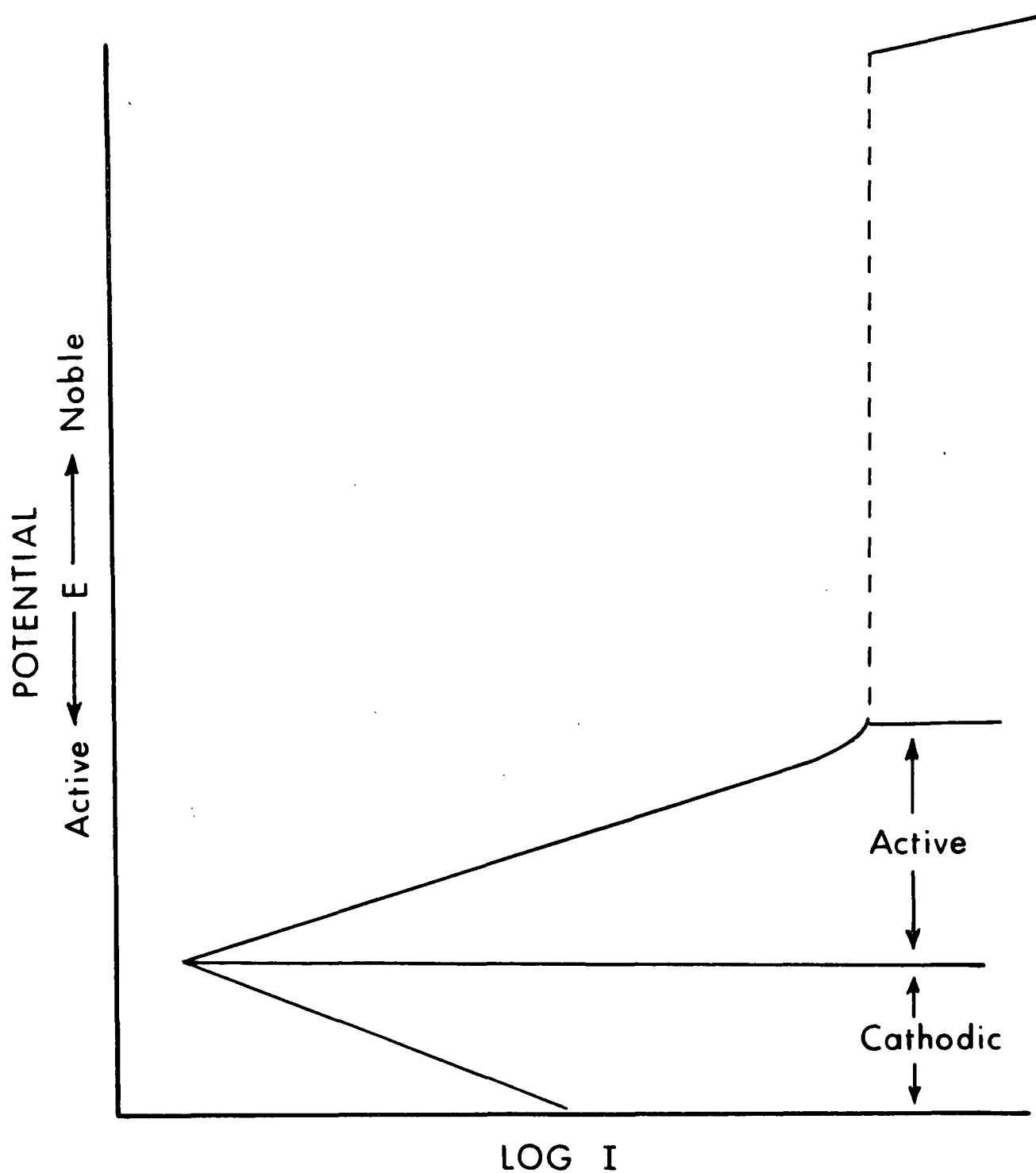


Figure 9. Galvanostatic Polarization Curve of an Active-passive Metal

WHITE LIQUOR

COMPOSITION

Part of the study conducted by Bowers (8) in Phase I of the kraft liquor corrosivity research program is concerned with gathering all possible information regarding the chemical composition of white liquor of different mills.

Table I displays the chemical composition of white liquor reported by the mills (8). The wide range of chemical compositions manifests the variations in recovery efficiencies and chemical make-ups as well as time and location of sampling. Table I also shows that most mills still operate at a sulfidity of less than 28%.

CORROSIVITY OF WHITE LIQUOR

This section is a review of the electrochemical characteristics of iron and steel in NaOH solutions in the absence and presence of various additives, followed by a review of the pertinent corrosion and electrochemical studies conducted in white liquor.

Electrochemical Behavior of Iron and Steel in NaOH Solution

Wensley and Charlton (MB) (7) investigated the anodic behavior of mild steel in NaOH solutions at 90°C. Their data, seen in Fig. 10, reveal two current density maxima. They assumed that at these maxima Fe(OH)_2 and Fe_3O_4 are formed by Reactions [1] and [2], respectively.

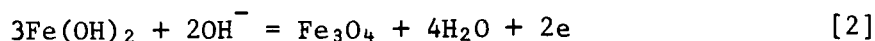
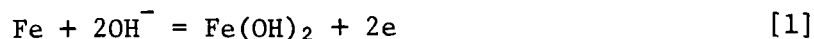


Figure 11 shows that the increase in alkali concentration shifts the anodic current density maxima toward higher magnitudes of current density. This behavior has

TABLE I^a

COMPOSITION OF WHITE LIQUOR
REPORTED BY THE MILLS
(g/L, Na₂O)

| NaOH | Na ₂ S | Na ₂ CO ₃ | Na ₂ SO ₄ | Percent Sulfidity |
|-------|-------------------|---------------------------------|---------------------------------|-------------------|
| 88.0 | 27.3 | 13.0 | 6.6 | 23.6 |
| 72.9 | 27.2 | 21.7 | -- | 27.2 |
| 88.0 | 23.0 | 24.0 | 8.0 | 20.7 |
| 99.5 | 34.0 | 54.0 | 11.8 | 25.4 |
| 71.0 | 39.0 | 20.0 | -- | 35.4 |
| 59.7 | 31.1 | 21.5 | -- | 34.2 |
| 80.1 | 19.2 | 19.2 | -- | 19.3 |
| 67.7 | 23.2 | 10.5 | 8.0 | 25.5 |
| 75.0 | 23.6 | 15.5 | -- | 23.9 |
| 114.0 | 32.0 | 34.0 | 13.6 | 21.9 |
| 78.7 | 27.3 | 27.3 | 7.6 | 25.7 |
| 75.5 | 27.2 | 20.8 | -- | 26.5 |

Other Compounds Reported

| Sulfite | Thiosulfate | Polysulfide | Chloride |
|---------|-------------|-------------|----------|
| 0.9 | 0.6 | 0.2 | -- |
| 5.5 | 2.4 | 20.7 | -- |
| -- | -- | -- | 5.8 |
| 1.5 | 2.6 | -- | -- |
| -- | 5.5 | 0.3 | 2.8 |
| -- | -- | -- | 2.2 |

^aTaken from Ref. (8).

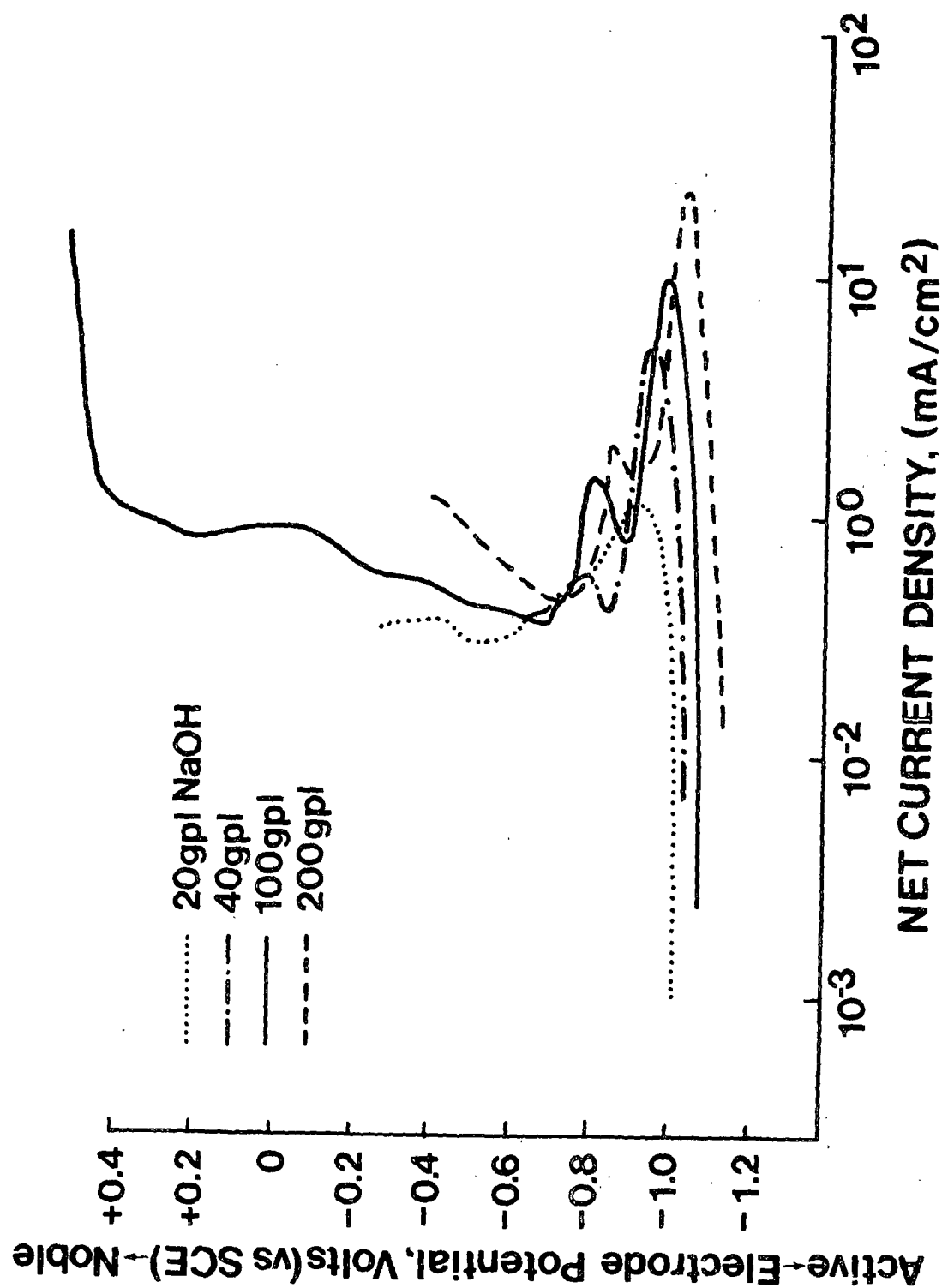


Figure 10. Anodic Potentiodynamic Scans of D. Wensley and R. Charlton for Mild Steel in NaOH Solutions of Various Concentrations at 90°C

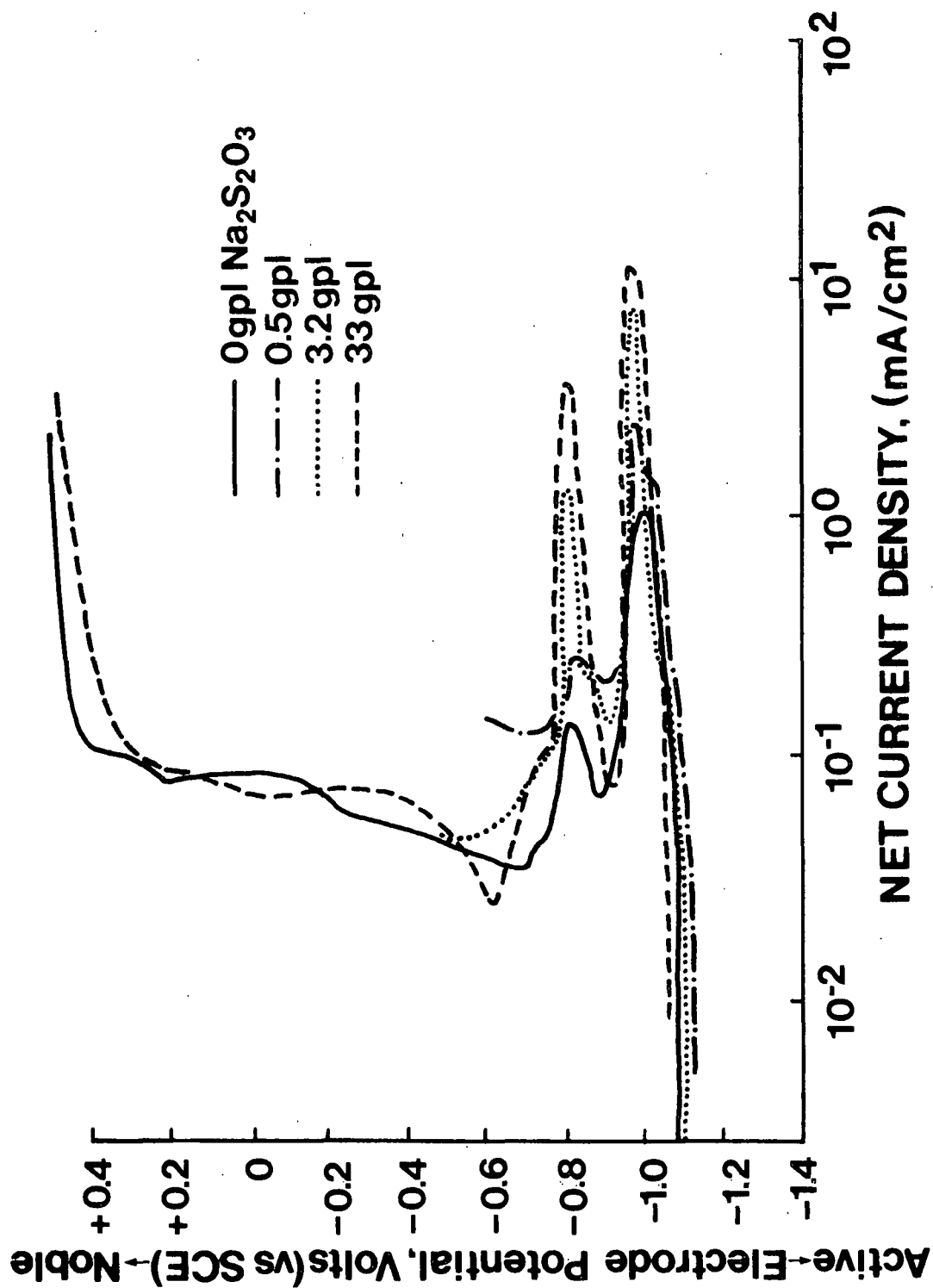


Figure 11. Anodic Potentiodynamic Scans of D. Wensley and R. Charlton for Mild Steel in 100 g/L NaOH Containing 0, 0.5, 3.2, and 33 g/L $\text{Na}_2\text{S}_2\text{O}_3$

been also observed by Jones, et al. (9). Wensley and Charlton (7) attributed the increase in current density maxima to a decrease in the ability of mild steel to be passivated at higher NaOH concentrations. Furthermore, it appears that the increase in NaOH concentration is also accompanied by a shift in the corrosion potential toward more active values (7). This is associated with an increase in the rate of steel dissolution within the active region (7). This could be due to the stability of the ionic species HFeO_2^- within the alkalinity and temperature ranges studied by Wensley and Charlton.

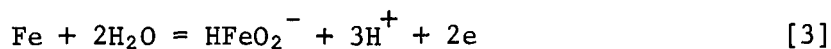
The nature of the passive film has been also studied by Foley, et al. (10). Using reflection and transmission diffraction, they indicated that the passive film formed on iron foils is composed of $\gamma\text{-Fe}_2\text{O}_3$ or possibly a mixture of $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 . Furthermore, the composition of the passive film was independent of the mode of passivation.

In 0.04M to 5M NaOH solutions and at 300°C, it was shown that the passive film on mild steel is composed of Fe_3O_4 (9). This oxide film is then converted to $\alpha\text{-Fe}_2\text{O}_3$ in the transpassive region. At concentrations lower than 0.04M NaOH, the transition of Fe_3O_4 to $\alpha\text{-Fe}_2\text{O}_3$ did not occur. Instead, cracklike pits appeared in the transpassive region.

Effect of Additives on the Electrochemical Behavior of Iron and Steel in Alkaline Media

This section reviews some of the studies performed on the effect of additives on the electrochemical characteristics of iron and steel in alkaline media. The anodic behavior of iron in deoxygenated 10^{-2}M Na_2S solution at $\text{pH} = 10.9$ and at 25°C was investigated by Bouet (11). In the passive region, two areas of passivation were observed. Each area was preceded by an anodic current density maximum. Bouet attributed the occurrence of the first area of passivation to the formation of FeS_2 . The second area was

attributed to the formation of $\gamma\text{-Fe}_2\text{O}_3$. Although the iron electrode was passivated, there appeared to be a residual current. This residual current is thought to account for the occurrence of the following reaction:



According to Pourbaix's (12) potential-pH diagram of iron at 25°C and Townsend (13), the stability region of HFeO_2^- is at pH values close to pH = 13 and at potentials more cathodic than the one observed by Bouet (11). This indicated that the occurrence of Reaction [3] in the passive region is not feasible as claimed by Bouet.

Using potentiodynamic techniques, Wensley and Charlton (7) studied the effect of $\text{Na}_2\text{S}_2\text{O}_3$, Na_2SO_3 , and Na_2SO_4 on the anodic polarization behavior of mild steel in 2.5M NaOH at 90°C. Figure 11 shows the anodic behavior of mild steel in 2.5M NaOH in the absence and presence of various concentrations of $\text{Na}_2\text{S}_2\text{O}_3$.

The effect of $\text{Na}_2\text{S}_2\text{O}_3$ appears to be mainly confined to the active region as well as to the current density maxima region preceding the passive region. To be more specific, $\text{Na}_2\text{S}_2\text{O}_3$ caused a change in the rate of iron dissolution which is not dependent on the increase in the $\text{Na}_2\text{S}_2\text{O}_3$ concentration. This change in the active region is accompanied by an increase in the values of current densities at the current density maxima. This might be attributed to competitive adsorption between OH^- ions and $\text{S}_2\text{O}_3^{2-}$. It seems that adsorption of $\text{S}_2\text{O}_3^{2-}$ on the steel surface increases the ease with which the ferrous ions enter into solution. In other words, $\text{S}_2\text{O}_3^{2-}$ adsorption facilitates the dissolution of the steel, therefore increasing the current value for anodic dissolution over the value prevailing when $\text{S}_2\text{O}_3^{2-}$ is not present. This would eventually lead to a continuous dissolution of the metal with the I_{crit} occurring at high values. The effect of $\text{S}_2\text{O}_3^{2-}$ seems to be analogous to the effect of chloride ions in preventing passivation of a metal or alloy (14). However, unlike chloride ions,

thiosulfate ions did not cause a breakdown in passivity of mild steel (2). The lack of breakdown is seen from the intact potential range and passive current density value of the passive region in Fig. 12.

The addition of Na_2SO_4 and Na_2SO_3 to 2.5M NaOH solution did not have any appreciable effect on the anodic behavior of mild steel at 90°C (7). Wensley and Charlton termed the role of Na_2SO_4 and Na_2SO_3 as being indifferent.

Electrochemical Behavior of Mild Steel in White Liquor

The anodic polarization curve of mild steel in NaOH solutions showed two distinct anodic current maxima (see Fig. 10). The addition of 2 g/L Na_2S to 100 g/L NaOH resulted in the appearance of a third current density maximum. Figure 12 shows that the third maximum is situated at a potential value more noble than the potential of the first maximum and more active than the second maximum. With further additions of Na_2S , the third maximum appears to increase in magnitude at a greater rate than the other two anodic current maxima, such that for Na_2S concentrations above 10 g/L, it became the critical current for passivation.

The passive range observed for mild steel in 100 g/L NaOH solutions seems to decrease with increasing Na_2S concentration (7). In 33 g/L Na_2S and 100 g/L NaOH solutions, which represents the concentrations range in typical white kraft liquor, the current breakaway was observed at -0.7 V versus SCE; whereas in 100 g/L NaOH the current breakaway was observed at +0.4 V versus SCE.

The corrosivity of white liquor in different mills was measured by the use of linear polarization (8). The linear polarization technique, also known as the polarization resistance technique, involves potential-current measurements near the corrosion potential. This technique was introduced by Stern and Geary (15). They devised a

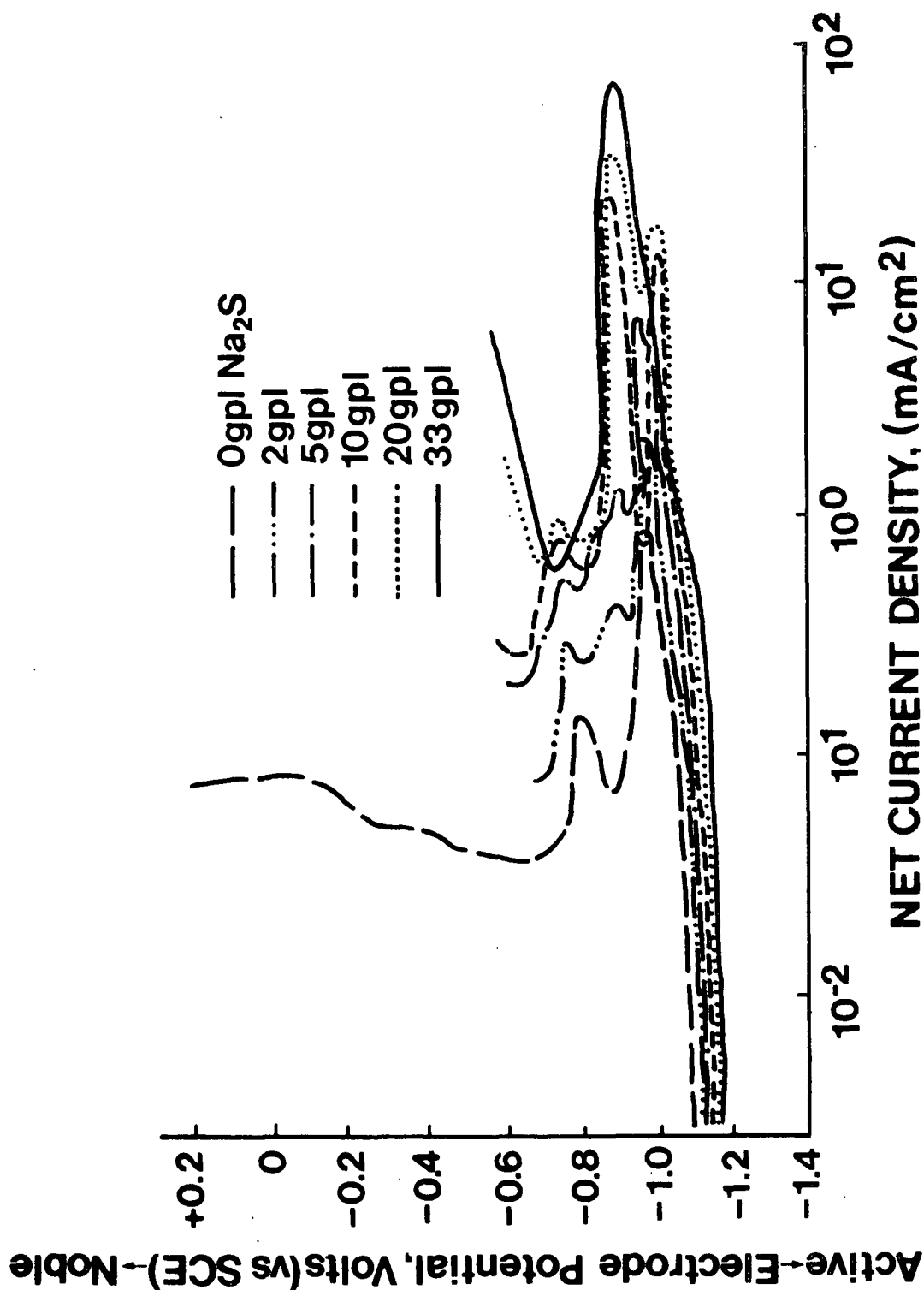


Figure 12. Anodic Potentiodynamic Scans of D. Wensley and R. Charlton for Mild Steel in 100 g/L NaOH Containing 0, 2, 5, 10, 20, and 33 g/L Na₂S

linear relationship between the overvoltage, η , and the applied current, I . The slope of the I - η linear region has the dimensions of resistance and is related to the corrosion current density, I_{corr} , by the following equation:

$$\frac{d\eta}{dI} = \frac{b_a b_c}{2.3 (b_a + b_c) I_{\text{corr}}}$$

where b_a and b_c are the anodic and cathodic Tafel slopes, respectively (see Appendix, p. 70 for derivation of the Tafel Slopes).

By using the linear polarization technique, Bowers conducted all measurements in white liquor with mild steel as the working electrode. The corrosion rate values are given in Table II. The high corrosion rates have been attributed by Bowers to turbulence encountered during the measurements, which impaired the complete formation of a surface film.

TABLE II^a
CORROSIVITY MEASUREMENTS IN WHITE LIQUOR

| Mill Code No. | Steady-State Corrosion Potential (MV, LAZ) | Corrosion Rate (mpy) |
|---------------------|-----------------------------------------------|-------------------------|
| 9 | -1020 | 12.0 |
| 18 | -870 | 8.0 _b |
| 21 | -1060 | 125.0 ^b |
| 22 | -- | -- |
| 23 | -915 | 300.0 ^c |
| 24 | -- | -- |
| 25 | +105 | 30.0 |
| 26 | -970 | Unstable |

^aTaken from Ref. (8).

^bInsufficient time in liquor to achieve steady state.

^cExtreme turbulence at this probe site cause a very high, noisy rate reading.

While investigating the differences in corrosion rates among different mills, Christiansen and Lathrop (16) observed the following: the corrosion rates changed from mill to mill along with white to black liquor ratios, and the corrosion rates for direct steamed digesters were different significantly from the rates noted for indirect heated digesters. Accordingly, Christiansen and Lathrop (16) concluded that the differences in corrosion rates from mill to mill could be related to differences in liquor corrosiveness. Based on their conclusion (16) and Stockman and Ruus' findings (17) that Na_2S , NaOH , and $\text{Na}_2\text{S}_2\text{O}_3$ are the ones contributing heavily to steel corrosion, the former authors put together these compounds in a mathematical model of corrosion expressed as:

$$C = -3.6 + 0.03 \text{ Na}_2\text{S} + 0.11 \text{ NaOH} + 0.04 (\text{Na}_2\text{S} \times \text{Na}_2\text{S}_2\text{O}_3),$$

where C is termed the liquor corrosiveness. This equation implies that NaOH and Na_2S affect corrosion independently of the other components, while the importance of $\text{Na}_2\text{S}_2\text{O}_3$ is dependent on the presence of Na_2S .

The work done by Wensley and Charlton (7) has shown a noteworthy result. The anodic polarization behavior of mild steel in white liquor showed that the effect of sulfide ions overshadowed the effect of thiosulfate. The separate and combined effects of S^{2-} and $\text{S}_2\text{O}_3^{2-}$ on the anodic polarization curve of steel in NaOH were compared and the dominant effect of sulfide over thiosulfate ions is shown. Figure 13 shows the anodic polarization curve of mild steel in white liquor and in 100 g/L NaOH containing 33 g/L Na_2S and 3.2 g/L $\text{Na}_2\text{S}_2\text{O}_3$. It appears as if there is a preferential adsorption of S^{2-} over $\text{S}_2\text{O}_3^{2-}$ onto the metal surface. It is also observed that the white liquor environment is causing slight inhibition of the anodic current density maximum in 100 g/L NaOH containing 33 g/L Na_2S .

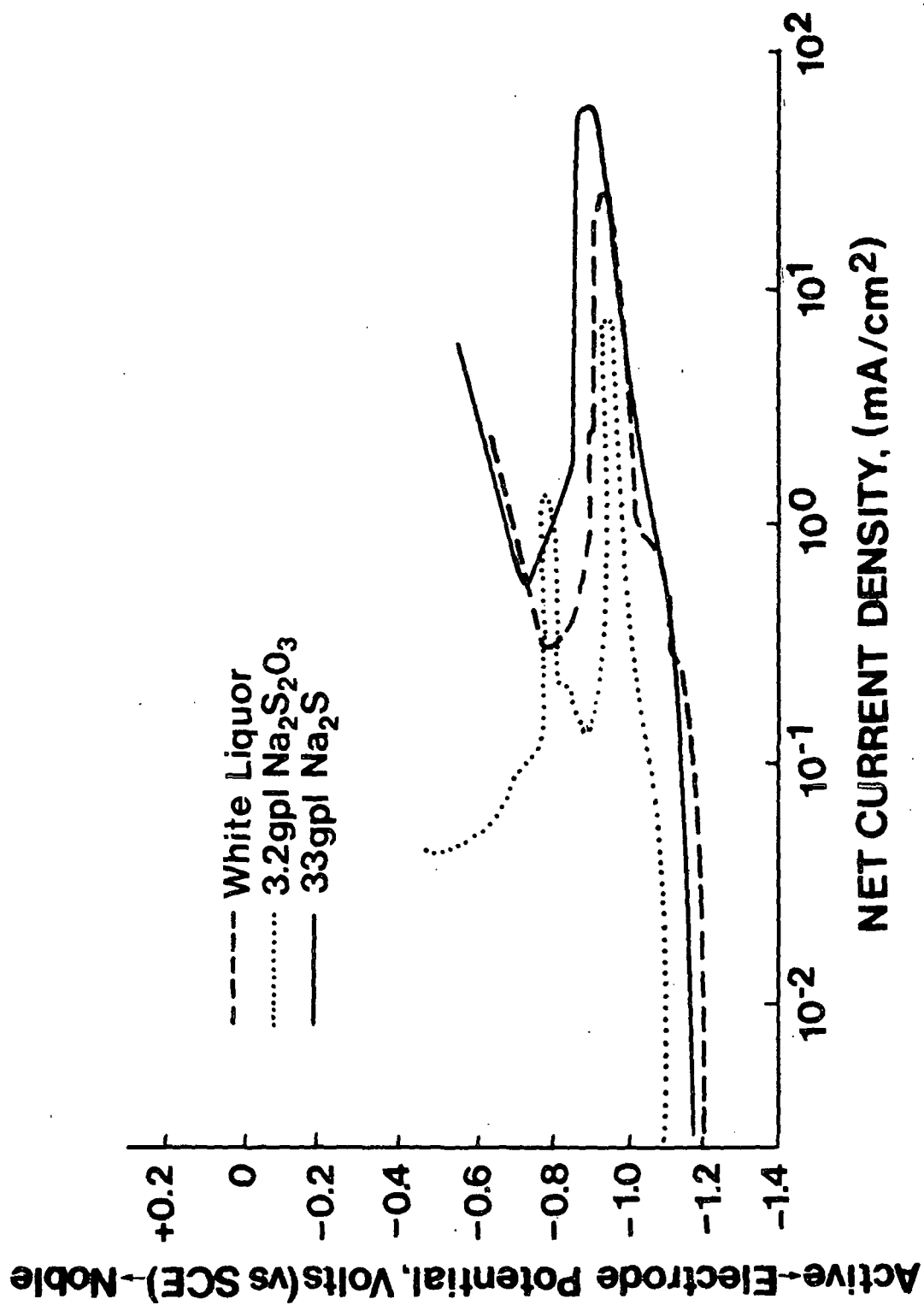


Figure 13. Anodic Potentiodynamic Scans of D. Wensley and R. Charlton for Mild Steel in White Liquor and in 100 g/L NaOH Containing 3.2 g/L Na₂S₂O₃ and 33 g/L Na₂S.

The experimental results in Mueller's work (18), Fig. 14, showed that the addition of $\text{Na}_2\text{S}_2\text{O}_3$ to white liquor increased the current density value for the anodic current density maximum. This maximum occurs at an approximate potential value of the critical current density maximum that is very pronounced at high sulfide concentrations in NaOH solutions as well as in white liquor. In simple words, the addition of $\text{S}_2\text{O}_3^{2-}$ to white liquor appears to enhance the effect of the sulfide ions on the anodic polarization behavior of steel.

Haegland and Roald (19) reported that the corrosion of steel in white liquor is controlled by the amount of polysulfide in the liquor. They implied that the polysulfide in white liquor resulted from the reaction between $\text{Na}_2\text{S}_2\text{O}_3$ and Na_2S according to:



Their data showed that the addition of Na_2SO_3 to white liquor increased the cathodic polarization. This increase was attributed to a decrease in the concentration of polysulfide. The reduction in the rate of the cathodic reaction was also exemplified by the shift of the electrode potential toward more negative potentials at a constant current (0.238 mA/cm^2) when Na_2SO_3 was added to white liquor containing $\text{Na}_2\text{S}_2\text{O}_3$. Any further additions of Na_2SO_3 increased further the shift in potential. This indicated that Na_2SO_3 inhibited the cathodic reaction.

However, the addition of $\text{Na}_2\text{S}_2\text{O}_3$ to white liquor showed a decrease in the cathodic polarization. This was attributed to the increase in polysulfide concentration according to the above-mentioned equation. The decrease in cathodic polarization was associated with an increase in corrosion rates. The corrosion rates were determined by weight-loss measurements and not by electrochemical means.

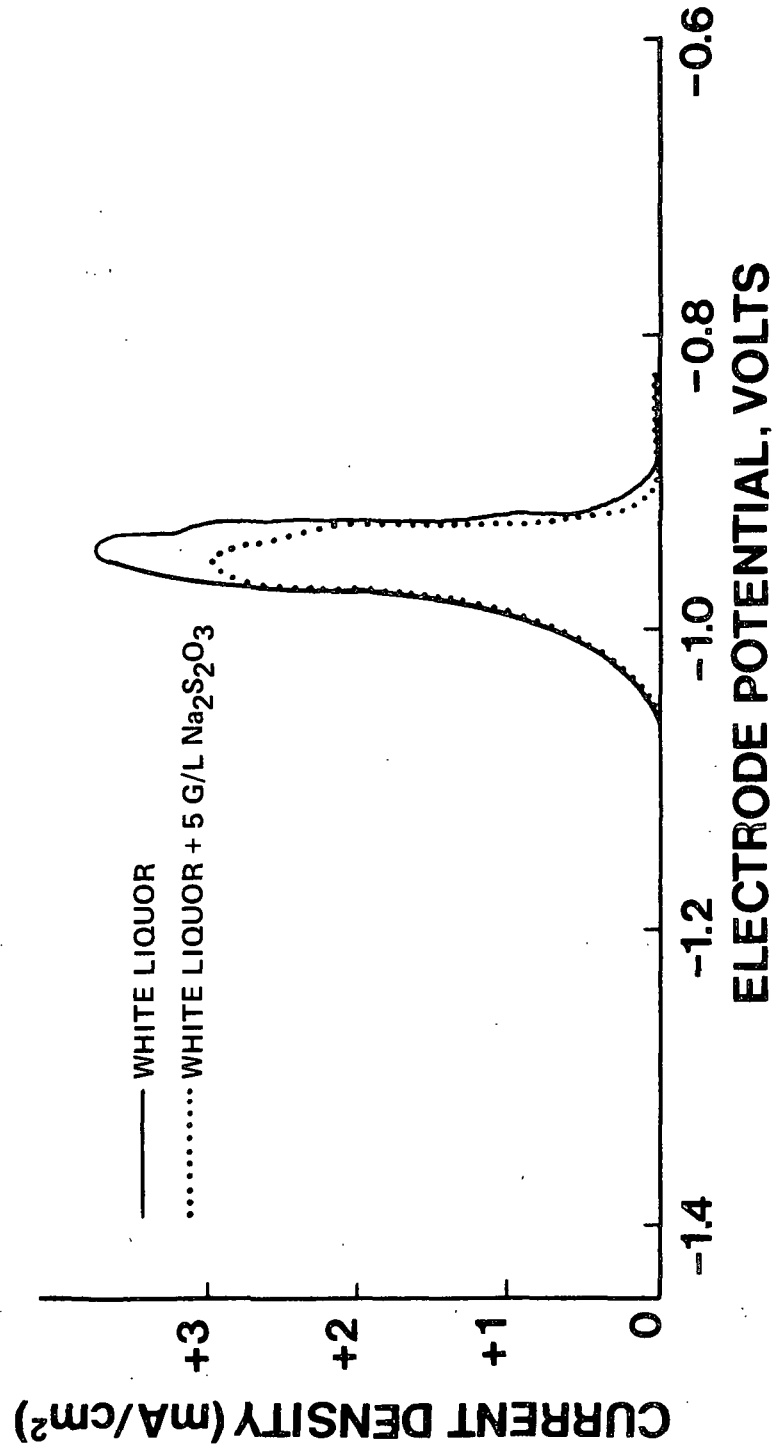


Figure 14. Polarization Curve of W. Mueller of Mild Steel in White Liquor with 0 and 5 g/L Addition of Na₂S₂O₃.

Also, by using weight-loss determinations, Hassler (5) found that the presence of small concentrations of polysulfide in white liquor caused an increase in the corrosion rate of mild steel. However, at high concentrations of polysulfide the corrosion rate of steel appeared to be negligible. This is in fact a typical behavior of an oxidizer.

The effect of an oxidizer on the electrochemical behavior of an active-passive metal may be described by Fig. 15. The anodic behavior of the metal is represented by curve $M \rightarrow M^+ + e$, and the cathodic behavior of the oxidizer is represented by curve $X + e \rightarrow X^-$. The intersection of the anodic and cathodic curves is designated by I_{corr} , which represents the corrosion rate of the metal. The potential corresponding to I_{corr} is designated by E_{corr} , which is called the corrosion, rest, or open-circuit potential.

Figure 15 also shows that the cathodic reaction of the oxidizer is under diffusion- or concentration-polarization control. This means that the rate of the reaction is controlled by transport or diffusion of the reacting species from the bulk of the solution to the electrode surface. The case of the oxidizer with diffusion control is chosen since it represents the electrochemical behavior of polysulfide on mild steel.

The effect of increasing oxidizer concentration on the corrosion rate of a metal is shown in Fig. 15. Curves 1, 2, 3, and 4 represent the cathodic polarization curve of the oxidizer at various concentrations, C_1 , C_2 , C_3 , and C_4 , where $C_1 < C_2 < C_3 < C_4$. Initially, (at C_1) the metal corrodes in the active state at a corrosion rate corresponding to point A. As the oxidizer concentration is increased from C_1 to C_2 , the corrosion rate increases from point A to point B. In this particular range of oxidizer concentrations, the metal acts like a nonpassivating metal, i.e., its corrosion rate increases with increase in concentration. At C_3 , the corrosion rate decreases

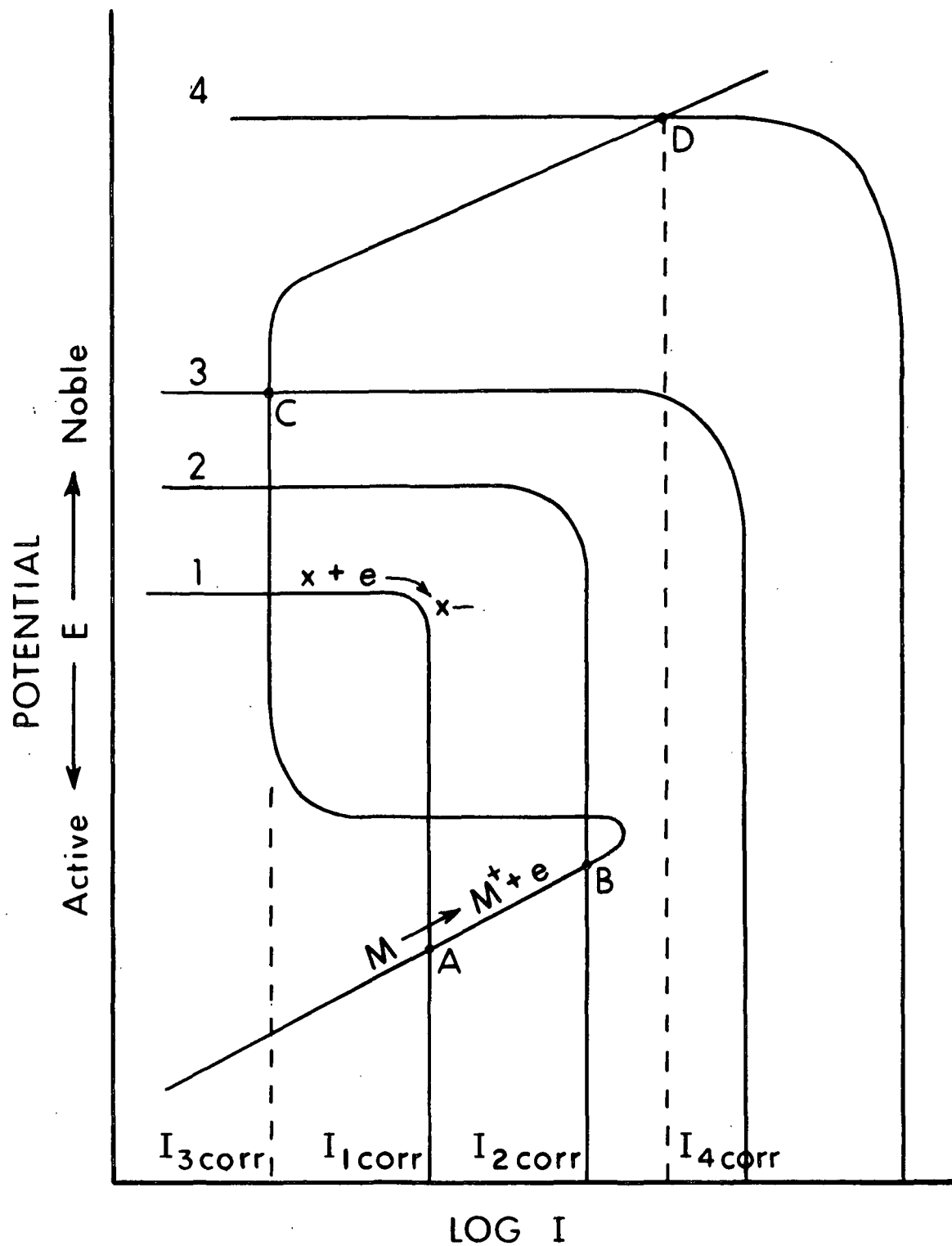


Figure 15. Effect of Oxidizer Concentration on the Active-passive Behavior of a Metal Under Diffusion Control

significantly from points B to C, and the metal is in the passive state. Now, as the concentration of oxidizer is increased further to C_4 , the transpassive region is intersected, and the corrosion rate increases again. The latter case may occur at higher concentrations of polysulfide. However no report of such an effect has been found. From Fig. 15 it can be seen also that the corrosion potential shifts to the noble direction with increase in oxidizer concentration.

Mueller (20) indicated that a passivating effect of polysulfide on carbon steel is obtained by the exposure of carbon steel to polysulfide liquor containing 2 to 5 g/L polysulfide. For stainless steel, the concentration of polysulfide required for passivation is much smaller than for carbon steel. However, no quantitative data were given in regard to stainless steel.

A very interesting work was published by Kessler and Bakken (21). They studied the effect of appreciable quantities of NaCl , Na_2SO_4 , and Na_2CO_3 on the corrosion rate of mild steel in white liquor. Their experimental results revealed that the effect of Na_2SO_4 , NaCl , and Na_2CO_3 is related to the amount of Na_2SO_3 in white liquor. The addition of any one of these chemicals to white liquor containing less than 1 g/L Na_2SO_3 decreased the anodic current maximum of the polarization curve, i.e., an inhibitive effect was experienced. On the other hand, the weight loss tests have indicated little effect of Na_2SO_4 , NaCl , and Na_2CO_3 on the corrosion rate of mild steel. However, at concentrations higher than 1 g/L Na_2SO_3 , the addition of any Na_2SO_4 , NaCl , or Na_2CO_3 caused an increase in the corrosion rate of mild steel.

Effect of Temperature on the Electrochemical Behavior of Iron and Steel

The increase in temperature tends to increase the critical anodic current density, I_{crit} , as can be seen from Fig. 16. An increase in I_{crit} indicates that the

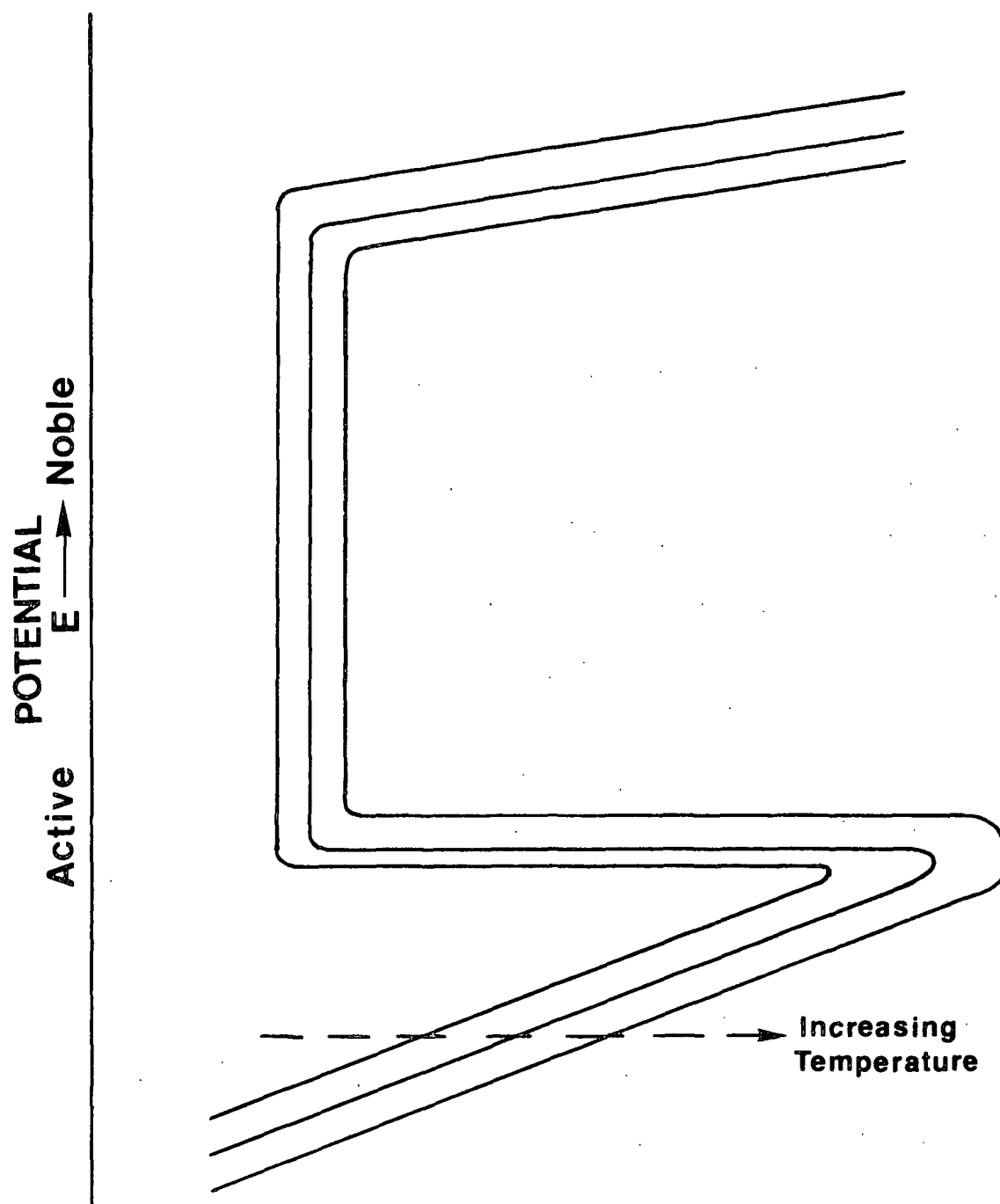


Figure 16. Effect of Temperature on the Anodic Dissolution Behavior of an Active-passive Metal

metal is prevented from being passivated. Usually the temperature has relatively little effect on the primary-passive potential and passive-dissolution rate (22).

Studies performed on the effect of temperature on the critical anodic current density of steel in white liquor indicate that the increase in temperature from 25° to 85°C caused an increase in the critical anodic current density (23). This result is consistent with Mueller's (18) experimental findings within the temperature range of 30° to 95°C.

When Banks, *et al.* (24) raised the temperature of white liquor and a mixture of white and black liquor (1:1 ratio) from 96 to 177°C, they observed a different behavior. They noted that the magnitude of the current density needed for obtaining passivity of mild steel coupons in white liquor and in a mixture of white and black liquor (1:1 ratio) decreased with rise in temperature from 96 to 177°C, as can be seen from Table III. This means that the rise in temperature within that range decreased the critical anodic current density of mild steel. This behavior may be attributed to the disappearance of some corrosive species or appearance of passivating species whose effects seems to overshadow the accelerating effect of the temperature.

The effect of temperature on the corrosion of iron in water containing dissolved oxygen presents a condition (case) where the temperature effect is overshadowed by the presence of the oxidizing species, oxygen (14). When corrosion is controlled by diffusion of oxygen, the corrosion rate at a given O₂ concentration approximately doubles for every 30°C rise in temperature. In an open vessel, where dissolved oxygen was allowed to escape, the rate increased with temperature to about 80°C and then fell to a very low value at the boiling point. The falling off of the corrosion above 80°C is related to a marked decrease of O₂ solubility in water as the temperature is raised. This effect seems to overcome the accelerating effect of

temperature alone. On the other hand, in a closed system, oxygen cannot escape, and the corrosion rate continues to increase with temperature until O_2 is consumed.

TABLE III^a

EFFECT OF TEMPERATURE ON CURRENT DENSITY FOR OBTAINING PASSIVITY OF MILD
STEEL COUPONS IN WHITE LIQUOR AND A 50/50 (v/v) WHITE AND BLACK
LIQUOR MIXTURE

| White Liquor | | White and Black Liquor Mixture | |
|--------------------|-----------------------------------------|--------------------------------|-----------------------------------------|
| Temperature, °F | Current Density, ma/in. ² | Temperature, °F | Current Density, ma/in. ² |
| 205 | 165 | 210 | 58 |
| 220 | 155 | 250 | 17 |
| 240 | 145 | 300 | 17 |
| 260 | 110 | 350 | 0 |
| 280 | 100 | | |
| 310 | 78 | | |
| 330 | 12 | | |
| 340 | 6 | | |
| 350 | 0 | | |

^aTaken from Ref. (24).

GREEN LIQUOR

COMPOSITION

Green liquor ideally should contain only sodium sulfide and sodium carbonate. However, a number of oxidized sulfur species are introduced into green liquor due to incomplete reduction in the recovery furnace associated with unavoidable liquor oxidation. Mueller (25) has shown that the rate of oxidation of green liquor is accelerated in the presence of Fe, Ni, and Mn ions.

The green liquor compositions reported by the mills are shown in Table IV. Table IV is extracted from Bowers' report on the corrosivity of kraft liquors (8). The differences in the green liquor composition were attributed by Bowers to the differences in sampling location and/or time of sampling.

CORROSIVITY

Using linear polarization technique, Bowers (8) measured the corrosion rates in green liquors of different mills using mild steel as the corroding electrode. The results indicate that liquor of similar analysis showed corrosion rates from 3 to 20 mpy. Furthermore, no relationship was observed between the corrosion rates and the corrosion potentials. In other words, the highest corrosion rate corresponded to the most noble corrosion potential, and vice versa.

It appears as if the corrosion rate data obtained in Bowers' work (8) are not entirely due to the dissolution of the metal. According to the mixed potential theory (see Appendix p. 70), the corrosion rate represents the summation of all partial anodic reactions occurring at the corrosion potential. The partial reactions may include the dissolution of the metal as well as the electrochemical oxidation of species in the environment of the metal.

TABLE IV^a

GREEN LIQUOR PROPERTIES REPORTED BY THE MILLS

| NaCO ₃ | Na ₂ S | Na ₂ SO ₄ | NaOH |
|-------------------|-------------------|---------------------------------|------|
| 69.4 | 27.9 | 6.6 | -- |
| 74.5 | 27.2 | 2.6 | 16.9 |
| 94.0 | 23.0 | 2.5 | -- |
| 88.1 | 29.3 | 16.2 | -- |
| 70.5 | 27.5 | 2.3 | -- |
| 80.0 | 25.0 | 7.0 | -- |
| 83.3 | 32.0 | 2.4 | -- |
| -- | 21.1 | -- | 19.2 |
| 76.9 | 24.6 | -- | 27.9 |
| 79.0 | 31.4 | 1.4 | -- |

Other Compounds Reported (g/L, Na₂O)
and Temperature

| Sulfite | Thiosulfate | Temperature Range (°F) |
|---------|-------------|---------------------------|
| -- | -- | 175-200 |
| -- | -- | 200-218 |
| 7.6 | 0.5 | 170-210 |
| 1.2 | 1.9 | 180-218 |
| 1.1 | 2.1 | 170-215 |
| -- | -- | 190-215 |
| -- | -- | 180-205 |
| -- | -- | 210 |

^aTaken from Ref. (8).

Mueller (25) related the corrosion of mild steel in green liquor systems to the thiosulfate/sulfide ratio. He further indicated that corrosion is usually encountered at liquor air interfaces, where sulfide is air oxidized to thiosulfate. Thus the product $[S_2O_3^{2-} \times S^{2-}]$ (see the corrosivity equation on page 28) is increased, and the solution becomes more aggressive in these parts of the liquor.

Although the sulfide ion oxidation is a slow process in aqueous solutions, Mueller (25) indicated that the reaction can be accelerated by the presence of various inorganic and organic catalysts such as Fe, Ni, and Mn ions. Organic catalysts may be tannin, gallic acid, hydroquinone, and pyrogallol. However, the effect of an organic catalyst is not expected to be important, since its presence in green liquor can occur by mere accident.

BLACK LIQUOR

This section reviews the chemistry of wood, the composition of the cooking kraft liquor, the reactions occurring between the cooking liquor and wood components, composition of black liquor, and, finally, the corrosivity of black liquor.

WOOD CHEMISTRY

The major components in wood are cellulose, hemicellulose, and lignins. The extractives and mineral constituents are the minor components of wood.

Cellulose is a polysaccharide composed of long linear chains of β -linked anhydroglucopyranose units. It is chemically classed as a glucan. The chains in native cellulose consist of as many as 10,000 glucose units. Due to the high degree of polymerization of cellulose, it is insoluble in water and aqueous alkalis. However, the chain size can be reduced by mechanical means or by hydrolysis, oxidation, or photochemical degradation. Boiling cellulose in dilute acids, e.g., 3 to 4% HCl or H_2SO_4 , would only partially attack it. However, in the presence of strong acids (72% H_2SO_4 or 41-42% HCl) cellulose hydrolyzes completely to celloextrins and finally to D-glucose.

Hemicelluloses are polysaccharides that accompany cellulose in plants. The most important polysaccharide polymers that comprise the hemicelluloses are galactoglucomannans and the glucoronoarabinoxylans. They have a slightly branched structure (or a linear anhydro-sugar backbone with side units). The degree of polymerization is only about 200 to 500 sugar units compared to 10,000 units in cellulose. The hemicelluloses are distinguished from the celluloses by their ease of hydrolysis in hot dilute acid solution and by their solubility in aqueous alkaline solutions.

Lignin is considered to be the aromatic polymer of wood. It is constituted from various phenylpropane units combined by C-C and/or C-O bonds in arbitrary sequences and in roughly correct proportions. Although a lot of research has been devoted to the determination of the structure of lignin, it still remains a mystery. Some interesting work regarding the structure of lignin can be found in Adler's (26), Gierers' (27), and Enkvist's, *et al.* (28) articles.

Lignin, also called the "encrusting substance of wood" is insoluble in water, in acids, and in common organic solvents. It is partly soluble in aqueous alkaline solutions and is readily attacked and solubilized by oxidizing agents. In the presence of strong mineral acids lignin undergoes condensation reactions. Details concerning lignin reactions can be found in books on wood chemistry, such as Rydholm (29) and Hägglund (30).

The extractives include low molecular weight compounds of various types. These compounds are extractable from wood with water or organic solvents.

From a physiological standpoint (29), wood extractives can be classified into the following groups: food reserves (fats, fatty acids), protectants (terpenes, resin acids, phenols), and plant hormones (phytosterols). According to their technical importance wood extractives can be divided into the following groups: terpenes, resins, and phenols. Although the former classification is more justified, the latter will be adopted in the context of this review.

The terpene content of the wood varies with species, generally from 0-2%. The terpenes are hydrocarbons which have the elementary composition $C_{10}H_{16}$ (monoterpenes), $C_{15}H_{24}$ (sesquiterpenes), or $C_{20}H_{32}$ (diterpenes). The monoterpenes are the most abundant. These are acyclic, monocyclic, and bicyclic terpenes, with the last two being more frequent. The most important bicyclic terpenes are α -pinene,

β -pinene, and Δ^3 -carene. Limonene and carvestrene are the dominating compounds among the monocyclic terpenes.

The "resins," as defined in the chemistry of pulping processes, are a variety of compounds that are less interrelated than the various terpenes. They include fats, fatty acids, resin acids, fatty alcohols, and phytosterols. Higher fatty alcohols and the phytosterols are commonly referred to as the unsaponifiable neutral substances or simply unsaponifiabiles.

The fatty acids are composed of saturated and unsaturated types having different molecular sizes. Analysis of total fatty acids in the ether extract of silver birch indicates that the unsaturated acids compose 81.7%, whereas the saturated ones constitute 18.3% of the total content (29). Linoleic, linolenic, and oleic acids are the most abundant among the unsaturated acids. They contain 18 carbon atoms, and their degree of unsaturation increases in the following order: oleic < linolenic < linoleic. Among the saturated fatty acids, palmitic (with 16 carbon atoms) and stearic acid (with 18 carbon atoms) are the dominating ones. The fatty acids are mostly present as triglycerides.

Levopimaric, neoabietic, and abietic acids are the most abundant resin acids present. The unsaponifiable neutral substances contain the higher fatty acids such as lignoceryl alcohol as well as plant hormones such as phytosterols, mainly β -sitosterol.

Phenols, extractable with alcohol or alcohol-benzene, consist of a large number of insufficiently studied compounds. The most important compounds in this category are: tannins, flavonones, stilbenes, and tropolones and their derivatives.

COMPOSITION OF THE COOKING LIQUOR

The white liquor as it arrives from the causticizers of the recovery system contains about 100 g/L Na_2O . Within the paper and pulp industry, the concentrations of NaOH and Na_2S are expressed in terms of Na_2O . When white liquor from the causticizer (100 g/L Na_2O) is added to the chips, excessive degradation of cellulose occurs. Therefore, the white liquor is first diluted with black liquor before it is added to the digester. Water is not used here as a diluent, as the water content is kept to a minimum for efficient chemical recovery.

The weight ratio of liquor to dry chips is on the average of 3 lb liquor per lb of wood. This ratio is frequently referred to as "liquor ratio."

REACTIONS BETWEEN COOKING LIQUOR AND WOOD COMPONENTS

The carbohydrate chemistry of the alkaline cooks involves a number of complicated reactions. As far as is known these reactions are not considerably affected by the presence of S-compounds (primarily Na_2S). Consequently, the carbohydrate reactions in both kraft and soda cooks should be of the same type. Some of the cooking liquor contains a considerable amount of polysulfide. In the presence of polysulfide, the yield of pulp is increased. This was attributed to the occurrence of a stopping reaction. The stopping reaction (as explained later) involves the oxidation of carbonyl groups which would otherwise act as starting points of degradation reactions.

It is known that degradation reactions of carbohydrates, primarily hemicelluloses, start at the aldehydic end groups and proceed along the chains in a sort of peeling reaction under conversion of the sugar monomers to saccharinic and other hydroxy acids. The peeling reaction would cease when a stopping reaction

takes place. The latter reaction would involve an intramolecular rearrangement which stabilizes the carbohydrate molecules by the formation of a carboxyl end group instead.

Other carbohydrate reactions to be considered are:

1. Alkaline swelling of the polymer which weakens the intramolecular forces, thereby facilitating reaction of the polymer with cooking liquor.
2. Alkaline dissolution of carbohydrate matter without its chemical degradation.
3. Alkaline hydrolysis of acetyl groups which results in the formation of acetate ions. Hydrolysis usually occurs at an early stage of the cook, probably immediately upon contact of the liquor with the wood chips.

As previously mentioned, lignin is constituted of various phenylpropane units combined by C-C and/or C-O bonds. During the cook, most of the C-C bonds are stable, whereas C-O bonds are cleaved to varying extents. Thus, carbon atoms carrying hydroxyl, alkoxyl, or aroxyl groups constitute the main sites of attack by the reactive species in the cooking liquors. This attack often results in fragmentation of lignin.

Unlike the carbohydrates, lignin is affected by the presence of sulfide ions in the cooking liquor. It was actually found that the presence of S^{2-} accelerates the rate of delignification with less damage to the cellulose and hemicellulose. The theory generally accepted postulates that the sulfide brings about sulfonation in the propane chains connecting the phenolic groups in the lignin molecule. Further reaction would then break the lignin molecule into smaller fragments whose sodium salts are soluble in the cooking liquor.

Thus, the action of hydroxide and sulfide can be summarized as follows:

the hydroxide ion is able to open up the alkylaryl ether bonds of lignin, and the degradation products thus formed are soluble in the medium. The sulfide accelerates the lignin dissolution, partly by reacting with some groups in lignin. The presence of sulfide blocks the condensation which otherwise would have been initiated. Also, during the reaction of lignin with sulfide ions, the alkyl aryl ether bonds are easily cleaved. According to Enkvist's chromatographic studies (28), the following compounds were found in original kraft liquor: C_6H_5OH , $C_6H_4(OH)_2(p)$, RH , $(HO)_2C_6H_3CHO(p)$, $RCHO$, $RCOOH$, $RCOCH_3$, $RCOC_2H_5$, $R \cdot CH_2CH_2OH$, $R \cdot CH_2COOH$, $RCH_2 \cdot CH_2 \cdot CH_2OH$, $R \cdot CH_2CH_2COOH$, $RCH=CHR$, and $HOC_6H_4 \cdot COOH$, where $R = \text{guaiacyl}(p)$.^{*} In pressure-heated kraft black liquor at 255 or 285°C in the presence of excess alkali the following products were found: $C_6H_4(OH)_2$, $CH_3C_6H_3(OH)_2$, $C_2H_5C_6H_3(OH)_2$, RH , $(HO)_2C_6H_3 \cdot CHO$, $RCHO$, $(HO)_2C_6H_3 \cdot CO \cdot CH_3$, $(HO)_2C_6H_3 \cdot CH_2 \cdot COOH$ (all p), and homoprotocatechuic acid.^{*}

From the relief gases of the kraft cook, the terpenes are recovered from the extractives as turpentine. Distillation of the kraft turpentine indicated three fractions:

1. A light fraction which constitutes about 5-10% of the crude turpentine and contains primarily methyl mercaptan and dimethyldisulfide.
2. A middle fraction which constitutes about 75% of the crude turpentine and contains α -pinene, β -pinene, Δ^3 -carene, and some dipentene and carvestene. These compounds are present in different proportions depending on the species of wood.
3. The heavy fraction which consists about 15% of the crude turpentine, contains sesquiterpenes, diterpenes, terpene alcohols, and some sulfur compounds.

^{*}The underlined substances are found in large amounts.

Reactions that might be encountered between the resins in the extractives and the cooking liquor are as follows:

1. Isomerization reactions which lead to a shift in the position of the double bond.
2. Dehydrogenation reactions which result in the increase of the degree of unsaturation in the compound. Due to dehydrogenation of abietic-type acids (31), dehydroabietic acid exists at a higher ratio in tall oil than in wood resins.
3. Alkali-hydrolysis reactions, which result in the hydrolysis of fats to glycerol and fatty acids.
4. Neutralization reactions, which result in the formation of sodium soaps from fatty and resin acids. This neutralization reaction renders the acids soluble, which is an important first step in the production of tall oil. Tall oil consists of about 50% fatty acids, about 40% resin acids, and some 10% unsaponifiables.

By vacuum distillation of the tall oil the following fractions are obtained

(29):

1. 10% Light oil containing neutral components and saturated fatty acids
2. 40% Fatty acid fraction consisting mainly of unsaturated acids
3. 20% Resin acid fraction containing mainly abietic acid.
4. 30% Pitch residue containing phytosterols, e.g., β -sitosterol

COMPOSITION OF BLACK LIQUOR

Tables V and VI display the possible organic by-products of the kraft cook. Generally, organic materials account for 55 to 70% of the total solids in black liquor.

TABLE V^a
BY-PRODUCTS OF THE KRAFT COOK

| Compound | Origin | Quantity, kg per ton of pulp |
|-------------------------------------------------------------------|--------------------------------------------------------------|------------------------------------|
| Methanol | Methoxyl groups of lignin and possibly glucuronoxylan | 5 |
| Acetate | Acetyl groups of the xylan as well as degraded carbohydrates | 100-200 |
| Formiate | Degradation of carbohydrates | 40 |
| Lactate | Degradation of carbohydrates | 100 |
| Saccharinic acids and lactones | Degradation of carbohydrates | 250 |
| Aliphatic sulfur compounds (methyl mercaptan, sulfide, disulfide) | Methoxyl groups of lignin and possibly glucuronoxylan | 1 |
| Turpentine | Terpenes | 8-10 |
| Tall oil (fatty and resin acid salts, phytosterols, etc.) | Wood resin components | 20-100 |
| Alkali lignin | Lignin | 400-600 |

^a Taken from Ref. (29).

Inorganic constituents include Na₂S, NaOH, Na₂CO₃, Na₂SO₄, Na₂S₂O₃, NaCl, and SiO₂. A possible composition of inorganic constituents in kraft black liquor is shown in Table VII. Depending on the degree of liquor oxidation in the recovery system, the concentration of sulfate and thiosulfate varies. The concentration of NaCl depends on the rate of liquor circulation as well as mill location. In some coastal mills, NaCl concentrations can reach 25 g/L.

TABLE VI^a

BY-PRODUCTS OF THE KRAFT COOK AND FROM SUBSEQUENT PRESSURE HEATING OF
THE BLACK LIQUOR WITH ALKALI AND SULFIDE AT 250-285°C

| Before Pressure Heating, kg ptp | | After Pressure Heating, kg ptp | |
|---------------------------------|-----|-----------------------------------------------------|-----|
| Tall oil | 50 | Acetic acid | 60 |
| Turpentine | 17 | Formic acid | 60 |
| Acetic acid | 40 | Methyl sulfide | 40 |
| Formic acid | 40 | Methyl mercaptan | 8 |
| Methanol | 5 | Pyrocatechol | 30 |
| Vanillin | 2 | Methyl catechol | 11 |
| Acetoguaiacone | 2 | Ethyl catechol | 9 |
| Guaiacol | 2 | Other ether-soluble phenols | 150 |
| Pyrocatechol | 1 | Homoprotocatechuic, protocatechuic and other phenol | |
| Other phenols | 42 | carboxylic acids, perhaps | 150 |
| Phenol carbonic acids | 45 | Ether soluble acids of carbohydrate origin | 150 |
| Nonvolatiles and lactic acids | 145 | Demethylated lignin of novalac properties | 100 |
| Total | 391 | Butanol-soluble lactones | 35 |
| | | Total | 803 |

^aTaken from Ref. (29).

TABLE VII^a

COMPOSITION OF SOUTHERN PINE KRAFT LIQUOR AT
22.9% TOTAL SOLIDS. ALL CONCENTRATIONS
ARE GIVEN IN g/L.

| pH | Na ₂ S | NaOH | Na ₂ CO ₃ | Na ₂ SO ₄ | Na ₂ S ₂ O ₃ | NaCl |
|------|-------------------|------|---------------------------------|---------------------------------|-----------------------------------------------|------|
| 11.6 | 4.86 | 6.78 | 55.85 | 2.01 | 14.28 | 0.17 |

^aTaken from Ref. (32).

CORROSIVITY OF BLACK LIQUOR

This review on the corrosivity of black liquor is concerned with the corrosive effect of black liquor as a whole, followed by the corrosive effect of organic compounds originating from wood products.

Mueller indicated that the addition of black liquor to white liquor affected the corrosiveness of the white liquor (12). The corrosiveness reaches a maximum near 50 or 60% black liquor. At higher percentages of black liquor, the corrosiveness of the black and white liquor mixture falls very rapidly to almost zero. At 70% black and 30% white liquor, the actual corrosion current was zero. The effect of the black liquor on the corrosion current appears analogous to the effect of an oxidizer on the active-passive behavior of a metal.

In a study on black liquor corrosivity by Bowers (8) during Phase I of the program "Corrosivity of Kraft Liquors," he found that the steady-state corrosion potentials were more noble in black liquor after oxidation than prior to oxidation. This should indicate a more stable and passive film formation. He also found that the corrosion rates in black liquor after oxidation at different mills were higher in one case and lower in another than the rate reported in black liquor before oxidation. Bowers indicated that this discrepancy could be due to the location at which the probe was installed for the corrosion rate measurements. In fact, he found that the probe that measured the low corrosion rate was installed in a low flow by-pass line after oxidation. Therefore, the high corrosion rate may be due to abrasion or disruption of newly formed surface (passive) films.

Black liquor oxidation, either before or after the liquor is concentrated, is now carried out in many mills. If the liquor is oxidized before

evaporation, H_2S and mercaptan losses in the evaporator are minimized. The oxidation of black liquor results in the oxidation of sulfide to thiosulfate. If the oxidation system is not operating efficiently, then sulfide would be only partially oxidized to $\text{S}_2\text{O}_3^{2-}$. This would lead to a high product of (S^{2-}) ($\text{S}_2\text{O}_3^{2-}$), and thus the solution environment becomes more aggressive according to Christiansen and Lathrop's (16) corrosivity equation.

Therefore, going back to Bowers' results, the increase in corrosion rate after black liquor oxidation compared to prior oxidation may then result from the inefficient oxidation procedures carried out in that mill. Further, the corrosion potentials listed in Table IX show that the potentials corresponding to low corrosion rates are more noble than the one corresponding to high corrosion rate. The more noble the potentials, the more oxidizing species are present in the environment.. This means that the more noble potential accompanying the low corrosion rates indicated that the concentration of $\text{Na}_2\text{S}_2\text{O}_3$ (oxidizing species) is higher than at less noble potentials. This further indicates that the oxidation procedure from S^{2-} to S_2O_3 may be more efficient at the mill with more noble potentials than at the other mill showing less noble potentials.

Thujaplicin, an isomeric isopropyltropolone, contributes to the corrosive attack on digesters (33). MacLean and Gardner (33) observed that thujaplicin in the free state or in aqueous or organic solvent solutions attacks metallic iron at room temperature. When a drop of thujaplicin oil is added to a piece of mild steel, a scarlet colored metal complex develops along with hydrogen evolution. Similarly, when iron filings were suspended in organic solvents of thujaplicin, they corroded with the development of a deep scarlet color. The attack by thujaplicin on iron has been attributed to the metal-complexing ability of thujaplicin (34). The development of the scarlet color is attributed to the formation of the soluble thujaplicin-iron

TABLE IX^a

CORROSIVITY MEASUREMENTS AND ANALYSES
AT LIQUOR SITES DESIGNATED BY THE MILL

| | Steady-State Corrosion Potential (MV, LAZ) | Corrosion Rate (mpy) |
|---------------------------------------------|--------------------------------------------------|----------------------------|
| Heavy black liquor after oxidation | -240 | 7.6 |
| Heavy black liquor prior to oxidation | -680 | 3.2 |
| Heavy black liquor storage- no oxidation | -- | 7.0 |
| Weak liquor after oxidation | -310 | 7.5 |
| Heavy black liquor after oxidation | -160 | 0.1 |

^aTaken from Ref. (8).

complex. On the other hand, MacLean and Gardner (33) reported that no weight loss of mild steel specimen was observed when the specimen was suspended in a refluxing alkaline solution of thujaplicin. This indicated that the organic metal complex is not stable in alkali. Since thujaplicins are steam distillable and their iron complexes are not stable in alkali, their corrosive effect would be expected to occur only in vapor space areas of the digester during the preparatory stages of the cook. The occurrence of accelerated corrosion of the dome of the digester was attributed by MacLean and Gardner to the presence of the steam-volatile thujaplicins.

MacLean and Gardner have also studied the effect of catechol, pyrogallol, dihydroquercetin, and taxifolin on the corrosion of mild steel. By applying weight

loss measurements, they observed that these phenolic compounds are active corroding agents in the presence of aqueous alkali. Their corrosive effect is due to their ability to form soluble organo-metallic complexes with iron. Their ability to form these complexes has been attributed to the presence of adjacent phenolic hydroxyl groups in the molecule. When one of the adjacent hydroxyl groups was blocked by methylation as in guaiacol, no increase in corrosion was noted. As a matter of fact, Hosokawa and Inui (35) reported that guaiacol and other lignin products inhibited the corrosion of iron and steel in solutions of pH higher than 3. The protective effect was accomplished by the formation of a compact and stable film on the electrode. Infrared absorption spectra have indicated that the film is composed largely of the lignin derivative.

Although catechol and taxifolin contain adjacent phenolic hydroxyl groups, MacLean and Gardner expected taxifolin to show less corrosion than catechol. This expectation was based on the greater molecular weight of taxifolin compared to catechol. However, the authors observed that taxifolin is 90% as corrosive as catechol on an equal weight basis. This indicated that other possibilities for metal chelation were present besides the dihydroxy groups. Taxifolin, which is a 3-hydroxy flavanone, is capable of undergoing a benzilic rearrangement (36). This rearrangement would lead to the formation of an α -hydroxy acid. α -Hydroxy acids are capable of forming iron complexes which are stable in alkali (33). It is then probable that the additional corrosivity of taxifolin is due to its degradation to the α -hydroxy acid in alkaline pulping (33). MacLean and Gardner have also reported that gluconic, glucuronic, and galacturonic acids, which are α -hydroxy acids, may cause dissolution of iron (33).

Mueller investigated the effect of dimethyldisulfide on the electrochemical behavior of mild steel in white liquor and in a mixture of white and black liquor at

a ratio of 1:1 (18). The addition of 1 to 4 g/L dimethyldisulfide to both types of liquors increased the rate of the cathodic reaction (18). Mueller proposed that the increase in the rate of the cathodic reaction is attributed to the occurrence of electrochemical reduction of dimethyldisulfide, analogous to the electrochemical reduction of cystine (37). In the white-to-black liquor mixture (ratio 1:1), the increase was almost proportional to the amount of dimethyldisulfide. Furthermore, Mueller's experimental results (18) revealed a pronounced increase in the anodic current maximum. This may indicate that dimethyldisulfide is decreasing the ability of mild steel to be passivated in the liquors. Therefore, dimethyldisulfide seems to play a dual role in interacting with both the anodic and cathodic polarization behavior of mild steel.

An interesting result came out of Mueller's investigation of the effect of pyrogallol on the corrosion current density of steel in NaOH with and without Na₂S (18). No significant increase in the corrosion current of steel was observed when pyrogallol was added to 100 g/L NaOH (2.5M). However, a significant increase in the corrosion current was noted when pyrogallol was added to white liquor (NaOH + Na₂S). Accordingly, Mueller suggested that pyrogallol increases the corrosion current by stimulating the corrosion reaction of Na₂S. In a later article, Mueller (18) suggested that the oxidation of Na₂S to Na₂S₂O₃ is found to be catalyzed by the presence of pyrogallol (38). Thus, the role of pyrogallol might be thought of as producing Na₂S₂O₃, which is known to contribute heavily to corrosion of steel. I suggest further study of the relationship between pyrogallol and Na₂S.

Some of the organic compounds in wood or formed during kraft liquor cooking of wood were found to exhibit inhibitive properties. Tannin was found to be important in protecting ferrous metals from both atmospheric and underground corrosion (39). Under certain conditions of boiler operations, it was reported that tannin forms a

blue-black layer of unknown composition on the internal surfaces of the boiler. This layer which helped to protect boiler surfaces from corroding was assumed to be composed of a tannin-iron complex (39). The formation of an organometallic compound from tannin and iron in alkaline solutions has also been proposed by Levin (40). Alkali metal tannates also have been found to inhibit the corrosion of ferrous materials (41). The fact that immersion of aluminum in tannin solutions led to the rapid formation of a protective layer suggested that tannins might also be used for the protection of nonferrous metals (42). Actually, Desai (43) found that among the most effective inhibitors of copper in NaOH solutions up to 1N are tannin and pyrogallol.

CONCLUSIONS AND DISCUSSION OF THE MOST SIGNIFICANT RESULTS

INORGANIC COMPONENTS OF KRAFT LIQUOR SYSTEMS

It has been shown that NaOH and Na₂S affect the corrosivity of kraft liquor independent of each other and also of the presence of other components (7). Increases in NaOH and Na₂S concentrations impair the ability of mild steel to become passive. This has been indicated by increases in the magnitude of the critical current density of steel.

The work done by Wensley and Charlton showed that Na₂S₂O₃ affects the anodic behavior of mild steel in NaOH solution (7). The mechanism by which S₂O₃²⁻ enhances the steel dissolution at such high alkaline concentrations has not been previously studied. A study of such a mechanism is considered to be a progressive step in defining and understanding the role of S₂O₃²⁻ in delaying the passivity of steel.

Another interesting result came out of the work of Wensley and Charlton. Their work on the anodic polarization behavior of steel in white liquor showed that the effect of sulfide ions overshadowed the effect of thiosulfate (7). It appears as if there is a preferential adsorption of S²⁻ over S₂O₃²⁻ onto the metal surface. It was also observed that white liquor caused a slight decrease in the magnitude of the anodic current density maximum in 100 g/L NaOH + 33 g/L Na₂S.

The correlation of the results of Wensley and Charlton's work with Haegland and Roald's work (19) shows that S₂²⁻ is neutralizing the effect of S₂O₃²⁻ and/or inhibiting the S²⁻ effect to a small extent.

Mueller showed that the addition of Na₂S₂O₃ to white liquor increased the current density for the anodic current density maximum (18). This maximum occurs at

an approximate potential value of the critical current density maximum, which is very pronounced at high sulfide concentrations in NaOH solutions as well as in white liquor (7).

In other words, the addition of $S_2O_3^{2-}$ to white liquor appears to increase the effect of the sulfide ions on the anodic polarization behavior of steel. This provides a very interesting feature to the relationship between the sulfide ions and thiosulfate ions, which needs to be investigated.

The correlation of Mueller's work (18) with Haegland and Roald's work, shows that S_2^{2-} and/or $S_2O_3^{2-}$ enhances the effect of S^{2-} on the anodic current density maximum of mild steel in white liquor. The enhancement of the corrosive effect of S^{2-} by S_2^{2-} and/or $S_2O_3^{2-}$ contradicts the conclusion drawn from correlating the work of Wensley and Charlton (7) with Haegland and Roald's (19). This contrast is a good foundation for developing a comprehensive and systematic study of the role of $S_2O_3^{2-}$, S^{2-} , and S_2^{2-} on the corrosion of steel.

ORGANIC COMPONENTS OF KRAFT LIQUOR SYSTEMS

There are few studies conducted on the corrosion and electrochemical behavior of mild steel in the presence of organic species originating from wood and from wood-cooking liquor interactions. The majority of these corrosion studies were conducted primarily by weight-loss measurements.

By using weight-loss determinations of mild steel, MacLean and Gardner were able to characterize the role of catechol in increasing the corrosion rate of steel. The corrosive action of the dihydroxy compound (catechol) was attributed to the presence of two adjacent hydroxy ions which give the organic compound the ability to form soluble complexes with iron (steel). Thus, by simple testing

coupled with a good grasp of organic, and organometallic chemistry, MacLean and Gardner were able to shed some light on the corrosive role of these and other organics (33).

The role of the organic compounds is sometimes not only confined to the formation of complexes leading to increased or decreased corrosion. A majority of the organic compounds are capable of undergoing electrochemical reduction or oxidation reactions which are also able to affect the corrosion of steel. Such electrochemical studies performed in the presence of the organics within the kraft liquor alkalinity and sulfidity ranges were, to my knowledge, only attempted by Mueller (18). He found that the addition of the dimethyldisulfide to white liquor increased the rate of the cathodic reaction as well as increased the value of the critical current density. The increase in the cathodic reaction was explained by the electrochemical reduction of dimethyldisulfide at the steel surface, whereas the increase in the value of the I_{crit} indicated the role of the organic in preventing or delaying the passivation of steel. However, the mechanism of intervention of dimethyldisulfide on facilitating the steel dissolution and increasing the value of I_{crit} has not been discussed.

The electrochemical study conducted by Mueller on pyrogallol in NaOH and white liquor showed that pyrogallol affects the corrosion rate of steel in the presence of S^{2-} ions, whereas in an NaOH solution, little change in the corrosion rate has been observed (18). Although this finding is very interesting, little attention has been directed to the understanding of the behavior of pyrogallol. The little attention that has been given to the role of the organic species in kraft liquor systems indicates the definite need for comprehensive fundamental studies in this practically unexplored area.

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NOMENCLATURE

| | |
|-------------------|-----------------------------------------------------------------|
| a_{ox} | activity of oxidized species |
| a_{Red} | activity of reduced species |
| α_a | charge transfer coefficient for the anodic reaction |
| α_c | charge transfer coefficient for the cathodic reaction |
| b_a | anodic Tafel slope |
| b_c | cathodic Tafel slope |
| C_B | bulk concentration of reacting species |
| D | diffusion coefficient of reacting species |
| δ | thickness of the diffusion layer |
| F | Faraday's constant |
| E | electrode potential |
| E_{corr} | open circuit potential; also called corrosion or rest potential |
| E_o | equilibrium potential |
| E_{pp} | primary passive potential or critical potential |
| I | current density |
| I_a | anodic current density |
| I_c | cathodic current density |
| I_{corr} | corrosion current density |
| I_{crit} | critical current density |
| I_L | limiting diffusion current density |
| I_o | exchange current density |
| I_T | total net current density |
| \xrightarrow{k} | rate constant of the anodic (oxidation) reaction |
| \xleftarrow{k} | rate constant of the cathodic (reduction) reaction |
| n | number of electrons transferred |

η overpotential
R gas constant
T absolute temperature
Zi reaction order with respect to the Z^{th} species

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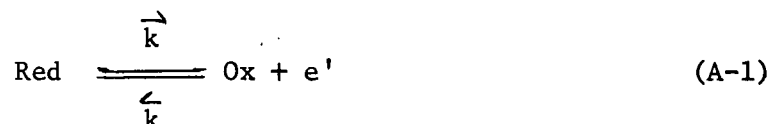
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APPENDIX

ELECTRODE KINETICS

In this section the electrochemical parameters pertinent to the activation controlled region will be derived.

A single step redox reaction can be represented by



where

Red is the reduced species

Ox is the oxidized species

\overrightarrow{k} and \overleftarrow{k} are the rate constants of the forward (oxidation) and backward (reduction) reactions, respectively

The net current density, I , at the electrode surface for the redox reaction can be written as:

$$I = I_a - I_c \quad (\text{A-2})$$

$$I = F k_a a_{\text{Red}} e^{\alpha_a \frac{FE}{RT}} - F k_c a_{\text{Ox}} e^{-\alpha_c \frac{FE}{RT}} \quad (\text{A-3})$$

where I_a and I_c are the current densities for the anodic (oxidation) and cathodic (reduction) reactions, respectively,

F is Faraday's constant

R is the gas constant

T is the absolute temperature

α_a and α_c are the charge transfer coefficients

a_{Red} and a_{Ox} are the activities of the reduced and oxidized species, respectively.

E is the electrode potential, i.e., the potential difference across the interface

When the redox reaction is in equilibrium, the net current density is equal to zero. The electrode potential at $I = 0$ is called the equilibrium potential, E_o . These equilibrium conditions can be expressed as:

$$\text{when } I = I_a - I_c = 0, \quad \text{then } E = E_o$$

$$\text{and } I_a = I_c = I_o$$

I_o is called the exchange current density and can be expressed as:

$$I_o = F k a_{\text{Red}} e^{\alpha_a \frac{FE_o}{RT}} \quad (\text{A-4})$$

or

$$I_o = F k a_{\text{ox}} e^{-\alpha_c \frac{FE_o}{RT}} \quad (\text{A-5})$$

Substitution of (A-4) and (A-5) into (A-3) gives the expression (A-6):

$$I = I_o \left\{ e^{\alpha_a \frac{F\eta}{RT}} - e^{-\alpha_c \frac{F\eta}{RT}} \right\} \quad (\text{A-6})$$

where η is called the overvoltage (overpotential) and is given by:

$$\eta = E - E_o$$

Equation (A-6) represents the classic form of the Butler-Volmer equation.

The derivation of Equation (A-6) has been so far restricted to a simple one-step redox process. Generally, corrosion involves two or more redox reactions occurring simultaneously at the metal-electrode surface. An analysis of a corrosion process can be made using the mixed potential theory.

The mixed potential theory is based on the assumption that the different reactions are independent of one another. Thus, the total net current, I_T , is equal to the summation of the anodic and cathodic current densities of all redox reactions, i.e., that

$$I_T = I_a - I_c = \sum_j I_{a,j} - \sum_j I_{c,j} \quad (A-7)$$

where $I_{a,j}$ is the anodic current density of the j^{th} partial process

$I_{c,j}$ is the cathodic current density of the j^{th} partial process

Because of the differences in equilibrium potentials and exchange current densities of the individual redox reactions, only one or two of the anodic and cathodic partial currents are significant to the total net current density.

A typical corrosion system can be seen in Fig. 17, in which two redox reactions are involved. Assuming that the most significant anodic current is given by the metal dissolution reaction ($I_a = I_{a,M}$) and the most significant cathodic current is given by the hydrogen evolution reaction ($I_c = I_{c,H}$), then the net current density can be expressed as:

$$I_T = I_{a,M} - I_{c,H} \quad (A-8)$$

and,

$$I_T = n_a F k_a \prod_i a_i^{Z_i} e^{\alpha_a \frac{FE}{RT}} - n_c F k_c \prod_m a_m^{Z_m} e^{-\alpha_c \frac{FE}{RT}} \quad (A-9)$$

where k_a and k_c are the anodic and cathodic rate constants, respectively

n_a and n_c are the number of electrons involved in the overall anodic and cathodic reactions, respectively

a_i is the activity of the species i which participates in the anodic reaction

a_m is the activity of the species m which participates in the cathodic reaction

Z_i is the reaction order of species i in the anodic reaction

Z_m is the reaction order of species m in the cathodic reaction

α_a and α_c are the charge transfer coefficients of the anodic and cathodic reactions, respectively.

The value of these charge transfer coefficients, α_a and α_c , depends on the respective anodic and cathodic mechanisms.

The potential at which the net current density, I_T , is equal to zero is called the open circuit, corrosion or rest potential, E_{corr} . At this potential the total anodic current density is equal to the total cathodic current density, and this current is called the corrosion current density, I_{corr} . This condition can be expressed as

$$I_{\text{corr}} = I_a = I_c \quad \text{at} \quad E = E_{\text{corr}}$$

Substitution of this condition into Equation (A-9) gives the expression (A-10):

$$I_T = I_{\text{corr}} \left[e^{\alpha_a \frac{F\eta}{RT}} - e^{-\alpha_c \frac{F\eta}{RT}} \right] \quad (\text{A-10})$$

where η , the overpotential, is given by:

$$\eta = E - E_{\text{corr}}$$

A-10 is the fundamental equation of metallic corrosion.

When the potential is far enough in the anodic (positive) direction ($\eta \gg RT/\alpha_c F$ or $\eta \gg E_{\text{corr}}$), the cathodic current density can be neglected in the

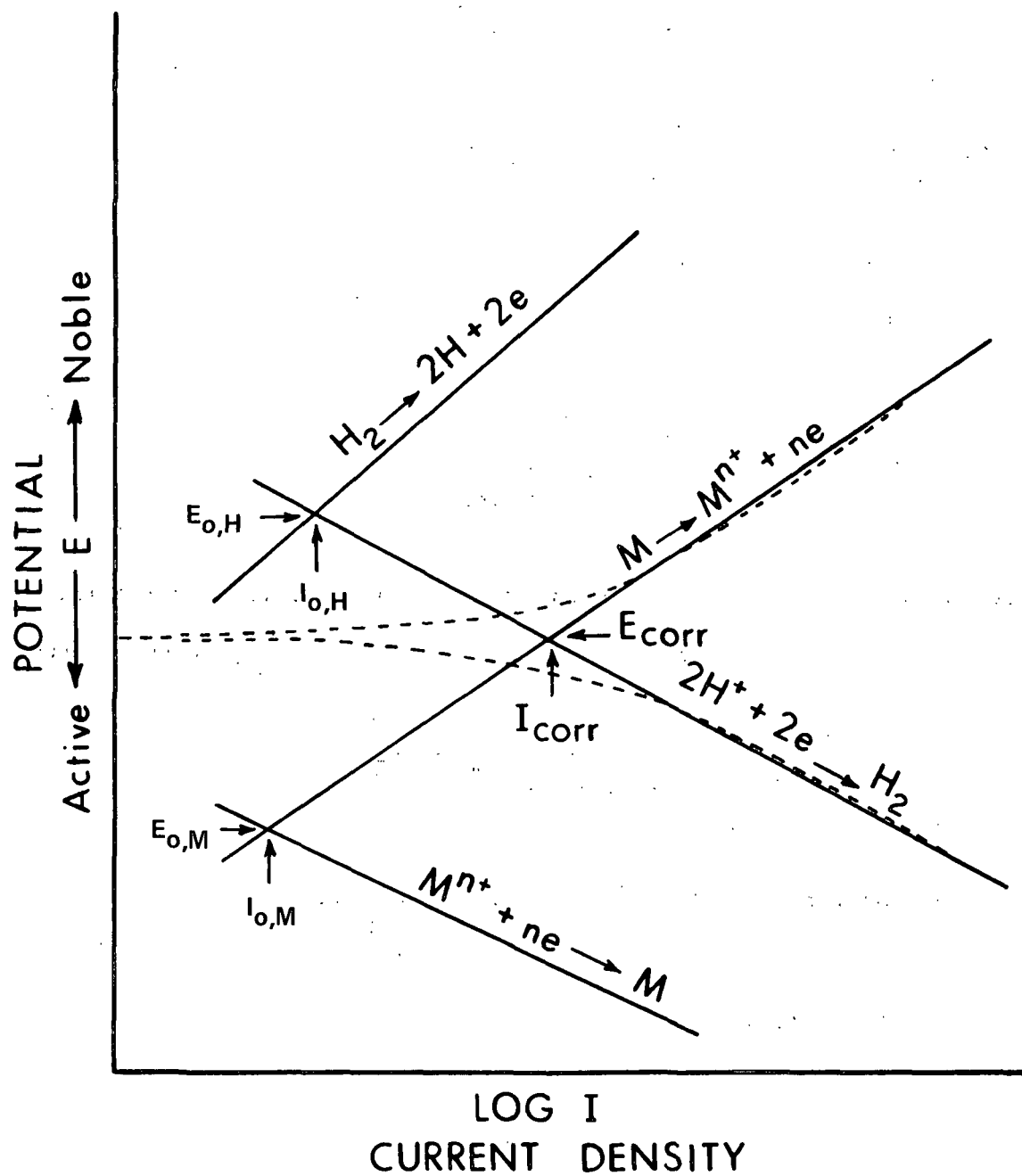


Figure 17. Schematic Diagram of a Typical Corrosion System Involving Two Redox Reactions

total net current. This leaves

$$I_T = I_A = n_A F k_A \prod_i a_i^{z_i} e^{\frac{\alpha_A F E}{RT}}$$

The anodic Tafel slope, b_a , and the reaction orders are then defined as

$$b_a = \left[\frac{\partial E}{\partial \log i_A} \right]_{a_i = \text{constant}} = \frac{2.303 RT}{\alpha_a F}$$

$$z_n = \left[\frac{\partial \log i_A}{\partial \log a_n} \right]_{E, a_{i \neq n}}$$

Likewise, when the potential is far enough in the cathodic (negative) direction ($-\eta \gg RT/\alpha_A F$ or $\eta \ll E_{\text{corr}}$), the anodic current density can be neglected. Hence

$$I_T = |I_c| = n_c F k_c \prod_m a_m^{z_m} e^{-\frac{\alpha_c F E}{RT}}$$

The cathodic Tafel slope, b_c , and the reaction orders are then:

$$b_c = \left[\frac{\partial E}{\partial \log |i_c|} \right]_{a_m = \text{constant}} = -\frac{2.303 RT}{\alpha_c F}$$

$$z_l = \left[\frac{\partial \log |i_c|}{\partial \log a_l} \right]_{E, a_{m \neq l}}$$